Liquid-Liquid Extraction of some Rare Earth Metal Ions by Polyoxyalkylene Systems

by

Abdul-Elah Ali Al-Naser

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

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This thesis, written by

ABDUL-ELAH ALI AL-NASER

Under the Direction of his thesis advisor and approved by thesis committee, has been presented and accepted by the Dean of the college of Graduate studies, in partial fulfillment of the requirement for the degree

MASTER OF SCIENCE IN CHEMISTRY

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Member

Prof. S. Sultan
Member

Chairman, Department of Chemistry

Dean, College of Graduate Studies

Date: 24-2-97

DEDICATION

This thesis is dedicated to my parents, my wife, my daughter, my son, my homeland Saudi Arabia and to its hard working people

ACKNOWLEDGMENT

Praise be to Allah, Lord of the Universe, may blessing and greeting be upon prophet Mohammed, his posterity, and his companions.

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Table of Contents

THESIS ABSTRACT

STUDENT NAME : Abdul-elah Ali Al-Naser

TITLE OF STUDY : Liquid-Liquid Extraction of Some Rare Earth Metal Ions by Polyoxyalkylene Systems

MAJOR FIELD : Chemistry

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Polyoxyalkylene systems, namely, polypropylene glycol(PPG-1025), polyethylene glycol(PEG-600) and polybutadieneoxide(PBDO-700) dissolved in either nitrobenzene or 1,2-dichloroethane have been tested as prospective extractants for some lanthanide metal ions (Pr^{3+}, Eu^{3+}, and Er^{3+}) from their aqueous solutions in the presence of picrate lipophilic anions. The metal ions were quantified before and after extraction using inductively coupled plasma emission spectrophotometry technique.

The percent extraction and the distribution coefficient have indicated that pH of the aqueous phase, picrate concentration and the organic solvent are the major parameters that affect the extraction efficiency of the metal ions. The optimum pH range was found to be 3.5 to 5.5 and the picrate concentration should be as high as possible, however a picrate concentration of about 0.05M proved to be adequate for a near quantitative extraction. In all cases, nitrobenzene enhanced a higher percent extraction compared to 1,2-dichloroethane.

The efficiency of the polyoxyalkylene systems to extract certain lanthanide metal ions was in the order PBDO-700 > PPG-1025 > PEG-600 when nitrobenzene was the organic solvent and in the order PPG-1025 > PBDO-700 > PEG-600 when 1,2-dichloroethane that has a lower dielectric constant, used as the solvent in the organic phase. The extractability of PPG-1025 towards the lanthanide metal ions was in the order $Pr^{3+} > Eu^{3+} > Er^{3+}$ irrespective of the organic solvent used.

The stoichiometry of the extracted polyoxyalkylene ion-pair with the lanthanide metal ions has been estimated. Each mole of the metal ions is associated with three moles of picrate anions and 13 to 14 moles of the propyleneoxide units in the case of PPG-1025, and about 10 moles of ethyleneoxide units in the case of PEG-600 and 10 moles of butadieneoxide units in the case of polybutadieneoxide-700.

Master of Science Degree
King Fahd University of Petroleum and Minerals
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June 1996

خلاصة الرساله

إسم الطالب : عبدالإله علي حسين آل نصر

عنوان الرساله: دراسه عمليه لإستخلاص أيونات العناصر الأرضيه النادره بواسطة مركبات بولي اوكسي الكايلين

التخصص : علم الكيمياء

تاريخ الدراسه: يونيه ١٩٩٦م

لقد تم إختيار فعالية مركبات بولي اوكسي الكايلين بعد إذابتها في نيتروبنزين أو ١،٢-ثنائي كلورو إيثان على إستخلاص بعض أيونات عناصر اللانثانيد البراسيديميوم+Pr3 واليوروبيوم+Eu3 والإيربيوم+Er3 من محاليلها المائيه بوجود أنيونات البكرات التي لها المقدره على إذابتها في المذيبات العضويه. ومركبات بولي اوكسي الكايلين التي أستخدمت هي: بولي إثيلين جلايكول-٦٠٠ (PEG-600) وبولي بروبيلين جلايكول- ١٠٢٥(PPG-1025) وبولي بيوتادايين أكسيد-٧٠٠(PBDO-700). كذلك تم تعيين كمية العناصر اللانثانيد قبل وبعد عملية الاستخلاص بإستخدام اسلوب مطيافية الإنبعاذ الذري بواسطة الحث البلازما المزدوج.

وقد أشارت كل من نسبة الإستخلاص ومعامل التوزيع للأنظمه المختلفه إلى أن العوامل المؤثره على كفاءة مركبات البولي اوكسي الكايلين في إستخلاص أيونات عناصر اللانثانيد هي قيمة رقم الهيدروجين وتركيز أيون البكرات في المحلول المائي وكذلك المذيب العضوي. ووجد أن قيمة رقم الهيدروجين المثلى هي في المدى ٣,٥ إلى ٥,٥ ، وإن تركيز البكرات يجب أن يكون أكبر مايمكن ٠,٠٥ مولار.

ووجد أن ٠,٠٥ مولار من محلول حمض البكريك تركيزا مناسبا للحصول على إستخلاص شبه كامل وبعد هذا التركيز من الصعب إذابة المزيد من حمض البكريك. وفي جميع الحالات وجد أن النيتروبنزين أكثر كفاءة في الإستخلاص من ١،٢-ثنائي كلورو إيثان.

هذا ووجد أن كفاءة مركبات بولي اوكسي ايثيلين لإستخلاص أيونات اللانثانيد تتدرج على الشكل PBDO-700 > PPG-1025 > PEG-600 عندما كان النيتروبنزين هو المذيب العضوي ووجد أيضا أن هذه الكفاءه تصبح على الشكل PPG-1025 > PBDO-700 > PEG-600 عندما يستخدم ١،٢-ثنائي كلورو إيثان كمذيب عضوي. وفي الوقت نفسه فإن كفاءة مركب بولي بروبلين جلايكول -١٠٢٥ لإستخلاص أيونات اللانثانيد تكون على النحو التالي $Pr^{3+} < Eu^{3+} < Er^{3+}$ بصرف النظر عن المذيب العضوي.

وتم أيضا تعيين نسب مكونات الأيونات الثلاثيه التي تتكون من بولي أوكسي الكايلين وأيون اللانثانيد وأيون البكرات. ووجد أن كل مول من الأيونات تتجمع مع ١٣ إلى ١٤ مولا من الوحدات البروبلين أكسيد في حالة PPG-1025 وحوالي ٩ إلى ١٠ مولات من وحدات الإيثيلين أكسيد في حالة PEG-600 و١٠ مولات من وحدات البيوتادايين أكسيد في حالة PBDO-700 .

درجة الماجستيرفي العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكه العربيه السعوديه

CHAPTER I

INTRODUCTION

1.1 Background

Development of suitable separation procedures for trivalent lanthanides from actinides has drawn the attention of analytical chemists since the advent of the nuclear industry. Their role in the disposal of nuclear waste to the environment was recognized during the early years of nuclear power production. Subsequently, this area received further momentum with the increasing application of trans uranium elements in industry and research. On the other hand, continued studies on the properties of lanthanide compounds have revealed their interesting application as laser materials, as catalysts and as shift reagents in nuclear magnetic resonance spectroscopy and magnetic hydrodynamics.[1]

Solvent extraction technique is one of the promising methods for separation of lanthanide metal ions. This technique depends mainly on the presence of an appropriate lipophilic anion, such as picrate, dipicrylaminate or thiocyanate, which is easily extractable to an organic phase containing an appropriate ligand [2]. Thus, the aqueous metal ion is transferred to the organic phase containing the ligand

forming ion-pairs and the degree of solubilization (extraction efficiency) could be taken as a measure for the complex formation efficiency.

The tendency of a large number of crown ethers (neutral carriers) to extract alkali and alkaline earth cations has been extensively studied[3,4], and in general, it was concluded from these studies that the selectivity sequence with alkali metals is $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ and with alkaline earth metals is $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

A little attention has been given to the studies on the efficiency of the polyoxyalkylene nonionic surfactants. It has been reported [5] that the extractability of heavy metal ions from their thiocyanate solutions by polyalkylene glycols increases in order of : $Co^{2+} > Fe^{2+} > Fe^{3+} > V^{4+} > Cu^+ > Hg^{2+} > Pb^{2+} > Ni^{2+}$. Also, extraction of alkali and alkaline earth metal ions into dichloromethane containing polyalkylene glycols has been studied by Jaber et al.[6] and the selectivity sequence for alkali and alkaline earth metal ions was found in the following orders: $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. Polyoxyalkylene compounds namely, polyethylene and polypropylene glycols have proved to be able to compete with crown ethers for their use as metal ion extractants and as active sensors in the membranes of ion selective electrodes in many instances, e.g.; tetraphenylborate salts of polyoxyalkylene complexes with some metal ions gave successful electrodes for the respective metal ions like Ba^{2+}, Sr^{2+}, Ca^{2+}, Li^+, Pb^{2+}, and La^{3+} [6,7] .

Stability and stoichiometry of the crown ether complexes with metal cations may depend mainly upon the relative sizes of the cation and the hole in the polyether ring, electrical charge on the ion, tendency of the ion to associate with the solvent, steric hindrance in the polyether ring and basicity of the oxygen atoms in the crown ether[8].

A vast number of crown ethers have been synthesized. Of all the crown ethers synthesized, benzo-15-crown-5 (B15C5) 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6) dicyclohexyl-18-crown-6 (DC18C6), dibenzo-24-crown-8 (DB24C8) and dibenzo-30-crown-6 (DB30C6) have been found to be the best ligands for alkali and alkaline earth cations [9] . Complexes of crown ethers with transition and heavy metals[10] (Ni, Co, Mn, Cd, Zn, Bi, UO_2, Ag) and uranyl salts[11] have also been isolated. Such crown ether-metal complexes are formed with various stoichiometries[12] but mainly with 1:1 (metal: crown) when the size of the cation more or less fits in the cavity of the crown. When the size of the cation exceeds the cavity size of the crown ether 1:2[13] or 2:3[14] complexes are formed. The large crown ethers have been shown to complex two metal cations simultaneously[15]. Usually in 1:1 complexes, the ring oxygens of the ligand arranged equatorially around the cation which remains exposed on the axial sides to the anionic species (the counter ion and or solvent molecules). Cations too small with respect to the cavity size of the crown may form complexes but the ligands tend to fold around the cation[16].

Polyalkylene glycols (open-chain polyethers) have shown a high tendency to interact with inorganic salts in spite of their complexes being less stable than those of macrocyclic polyethers[17]. The lower stability of the complexes with acyclic polyethers might be attributed to the macrocyclic effect[18] since entropic forces work against encapsulation of the cation by the acyclic polyethers[9].

Polyethylene glycols (PEG) were found to form crystalline complexes with mercury(II) halides, where the ratio of monomeric ethylene oxide units (EOUs) is 4:1 for chloride complexes but 5:1 for iodide[19]. Polyglycol dialkylethers (glymes) $RO(CH_2CH_2O)_nR$ where R is CH_3 or C_2H_5 and n is 4 or 6, form crystalline complexes with mercury (II) chloride with a stoichiometry of 4 EOU:1$HgCl_2$ and 6EOU:2$HgCl_2$ regardless of the alkyl group[20]. Polyethylene glycols and their nonylphenol adducts (NP) and polypropylene glycols (PPG) using a large anion such as tetraphenylborate (TPB) form complexes in the presence of barium, strontium or sodium ions[6]. The stoichiometry of barium complexes with PEG, nonylphenol adducts of PEG and PPG in the presence of NaTPB was found to be:

~10.5	EOUs	:	M^{2+}	:	2TPB for	PEGs
12	EOUs	:	M^{2+}	:	2TPB for	NPs
12	POUs	:	M^{2+}	:	2TPB for	PPGs
~8.5	EOUs	:	M^{2+}	:	TPB for	PEG, and PPG.

It has been claimed that one salt molecule of alkali metal ions (K, Rb, or Cs halides) associates with about 9 EOUs when they complex with PEGs[21]. However NaSCN and KSCN as well as NaI have been found to form highly crystalline complexes with poly(ethylene oxide) systems in methanolic solution with stoichiometry of 1:4 (metal ion:EOUs). Also PEG of ethylene oxide units have formed a long range of crystalline complexes with alkali and alkaline earth cations[22]. Generally speaking, studies have confirmed that the interaction between the metal cations and the oxygen atoms of the polyalkylene glycols causes the complex formation, a fact that is consistent with the principle of complex formation by the cyclic polyethers.

Extraction of U(VI) by dialkyl phosphoric acid into an organic solvent was enhanced by addition of a neutral organophosphorous compound such as trialkyl phosphates[23]. The efficiency of the mixed reagents for extraction is greater than either of them alone. This combined action is termed synergism. The synergistic enhancement has been attributed to a combined effect of the two active species, the acid (HX) which neutralizes the charge on the cation and the other species which removes any water in the coordination sphere of the extracted cation[23]. The coordinating species should not be hydrophilic and the bond strength with the cation is less than that with HX. The interaction should saturate the maximum coordination number of the cation and should give the preferable geometry[24]. Healy[24] reported the synergetic extraction of uranium (VI), thorium, lanthanides (III), actinides (III)

and alkaline earth metals with thionyltrifluroacetone-tributylphosphate, thionyltrifluroacetone-tributylphosphine oxide and thionyltrifluroacetone-triphenylphosphate. Healy[24] also observed that the synergetic effect increases with increasing basicity of the ester i.e. tri-n-octylphosphine oxide> tributylphosphate> triphenylphosphate.

Some lanthanide metal ions have been extracted by mono-(2-ethylhexyl)phosphoric acid-n-decanol system[24]. In a system like this, it was found that the excess of the solvent reduces the concentration of free chelating agent by increasing the interaction between HX and solvent through hydrogen bonding leading to smaller extraction coefficient[24]. This effect has been called antisynergism.

Systems like N-benzoyl-N-phenylhydroxylamine[25] and halogen acetic acid in di-n-butylphosphoric acid, or nitrophenols instead of halogen acetic acid were used in hafinium (IV) extraction. The synergetic effect in these systems is attributed to hydrogen bonding.

Another type of synergism was reported by Rais et al[26] in which he studied the extraction of alkali and alkaline earth dipicrylaminates into nitrobenzene using polyethylene glycol as synergetic agents. The synergetic factor(S) which is the maximum distribution ratio of the element in the presence of the synergetic agent to

that in its absence $\left(S = \frac{D_{max}}{D_o}\right)$ was 10^3 in the case of Sr^{2+} PEG (400) extraction system. The synergism is attributed to the hydrophobic effect of the ethylene (-CH_2-CH_2-) units in polyethylene glycol which lipophilizes the cation.

The synergism of polyethylene glycols in the metal ion extraction was found to be dependent upon molecular weight of the glycol[26]. The maximum synergism was found for polyethylene glycol 400.

1.2 General Principles of Liquid-Liquid Extraction

Solvent extraction enjoys a favored position among separation techniques because of its ease, simplicity, and wide scope. Separation by extraction can usually be accomplished in a few minutes using a simple pear-shaped separatory funnel, or an ordinary stoppered centrifuge tube and the solvent layers separated by centrifugation. It is applicable both to trace level impurities and to major constituents. Furthermore, inorganic constituents are often separated in a form suitable for direct analysis by spectrophotometric, atomic absorption or emission, radiochemical or other techniques[27,28].

In solvent extraction, a solute of interest transfers from one solvent into a second solvent that is essentially immiscible with the first. The extent of transfer can be varied from negligible to essentially total extraction through control of the experimental conditions. This transfer is an equilibrium process in which it is impossible to extract every single molecule or ion pair from one phase to the second. The extent of the transfer of a solute from one phase into the second is designated as distribution or partition coefficient which could be expressed as D[23,29].

Thus:

$D = \frac{[A]^*}{[A]} \frac{\delta^*_A}{\delta_A}$, where [A] and [A]* are the concentration of A in the aqueous phase and the organic phase respectively, δ_A and δ^*_A are the aqueous and the organic activity coefficient of A respectively. Distribution or partition coefficient expression deals with distribution of only a single species of the same component e.g. component A. From a practical point of view, it is more convenient to measure the total concentration of all species of the same component in each phase rather than measuring the concentration of a specific molecular form. Thus the distribution ratio (D) term has been expressed as follows[29],

$$D = \frac{C^*_A}{C_A}$$

where C^*_A and C_A designate the total concentration of all species of A in the organic and aqueous phases respectively, assuming the activity coefficient to be unity. The magnitude of D is the factor which determines the completeness of extraction, when D

is very large it is possible to remove component A quantitatively from the aqueous phase by a single extraction. Generally, an extraction is considered quantitative if it is at least about 99.9% complete. The amount of material that will remain unextracted could be expressed by the equation[30].

$$C_A = C_A^o\left[\frac{V}{DV^*+V}\right]^n$$

where C_A^o and C_A are the initial and equilibrium concentrations of A respectively after n extractions, V, V* are the volumes of aqueous and organic phases respectively. For a single extraction n is 1.

In multi-component system, the magnitude of D for each constituent is the major criteria which affects the separation of various components. The effectiveness of separation may be expressed in terms of the separation coefficient or factor (α)[29] which is related to the distribution ratios as follows:

$$\alpha = \frac{D_A}{D_B}$$

where D_A and D_B are the distribution ratios of a mixture components A and B. The larger the magnitude of α the more the selectivity of the extraction system towards component A over component B. In order to recover one component without the other, various techniques may be applied to suppress the extraction of the unwanted

component like, e.g. varying the solvent properties which are of interest to extraction such as, boiling point, viscosity, dielectric constant, density, flammability and toxicity[31].

1.3 Extraction of Metal Ions

Metal ions don't dissolve appreciably in organic solvents of low Polarity but they are readily soluble in water. The higher solubility in water is attributed to its high dielectric constant. Thus, water molecules are capable of disrupting the lattice of metal salts. Water also tends to solvate the metal ions by coordination. In order to effect transfer of metal ions from the aqueous to the organic layer, it is necessary to free the water molecules in its hydration sphere and to convert it to an electrically neutral species. Charge neutrality reduces electrostatic interaction between solute and water and hence lowers its aqueous solubility or enhances its organic extractibility.

The uncharged extractable metal species can be formed in a great variety of ways, which could be considered as the principle upon which the extraction systems are classified. Simply, extraction systems might be classified into the following types[32].

1.3.1 Covalent-Neutral Molecules Extraction Systems

The solute is mostly a neutral molecule which is not hydrated to any appreciable extent e.g. I_2, $GeCl_4$. The organic solvent dissolves the transferred solute but does not react with it chemically.

1.3.2 Uncharged Metal Chelates Extraction System

The metal ion complexes with a polydentate ligand which is capable of simultaneously filling all the coordination sites of the ion and neutralizing its positive electrical charge. The ligand may be considered as a weak acid whose anion can participate in charge neutralization and contain hydrophobic groups to reduce the aqueous solubility of the complex, e.g. acetylacetone useful for alkali metals[30].

1.3.3 Ion Association Extraction System

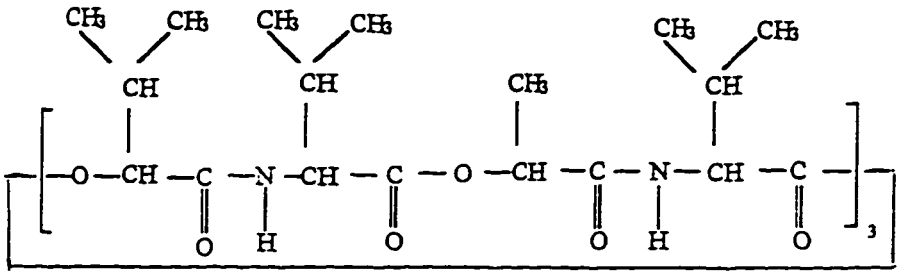
The metal ion is incorporated into a bulky molecule and the resulting charged species is associated with another ion of an opposite charge to form a complex that is electrically neutral. Also the metal ion might associate with a large counter ion without actual bond formation. Ion association may be categorized into the following: 1) Non-chelating complex, 2) chelated complexes, and 3) Oxonium system.

1.4 Neutral Carriers (Neutral Macromolecules) and their Ion Binding Properties

Neutral carriers are mainly uncharged molecules either containing cavities (macrocyclic molecules) in which a cation can be accommodated or having the ability to wrap around the cation (noncyclic macromolecules) forming charged ligand-cation complex. Such complexation enhance the solubility of the cations in the organic phase. Great attention has been given to such compounds since they selectively bind the metal cations, thus they gain their importance in analytical chemistry. The ability of the cyclic or noncyclic macromolecules to bind cations is related to the lone pair electrons of the donor oxygens of the molecules where the cation is held by electrostatic attraction between the negatively charged oxygens of the C-O dipoles and the cation[8,9,14,33]. Many reports have been published concerning the properties, preparation and analytical role of such neutral macromolecules as electrochemical active materials in the membranes of ion selective electrode[34] and as quantitative extractants for particular metal ion from matrices of other ions[35].

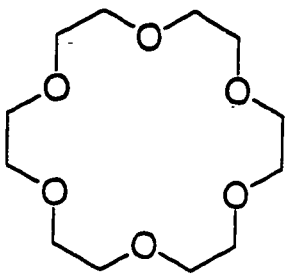
Generally, macrocyclic compounds of analytical interests can be classified as follows:

a) Macrocyclic antibiotics e.g., valinomycin

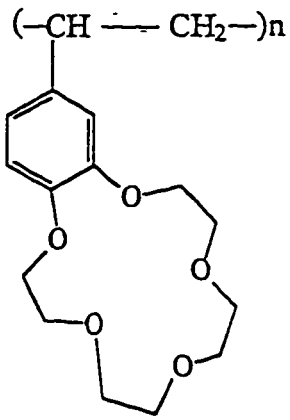


b) Crown Ethers (macrocyclicpolyethers) which have the basic structure[8,9,18,33,34]

$-[-CH_3-CH_2-O-]_n-$, for example 18-crown-6



Where 18 refers to the number of ring members and 6 denotes the number of heterocyclic oxygens. Sometimes oxygen atoms are completely or partly replaced with nitrogen (aza crowns) or with sulfur (sulfa crowns). Poly (crown ethers) also have been synthesized e.g., poly (vinylbenzocrown ether)



Poly (vinyl benzo crown ether)

c) Non cyclic polyethers which are the open-chain analogues of the macrocyclic polyethers, for example, polyalkyleneglycols (polyethylene glycols, polypropyleneglycol and their derivatives).

1.5 Inductively Coupled Plasma Atomic Emission Spectroscopy, ICPAES

ICP-AES is an established technique for element analysis at the trace, minor and major levels. The potential for using the ICP-AES as an excitation source was first recognized by Greenfield and Fassel in 1964 but a further 10 years of active research was required before the availability of commercial equipment encouraged wide spread use. Note worthy features of the technique include the applicability to metals and non-metals, a high sensitivity for elements under a single set of operating condition, simultaneous multi-element analysis capability, a wide dynamic range and a relative freedom from inter-element matrix effects[36].

The ICP-AES source is formed by the coupling of a flowing stream of ionized argon gas with a powerful radio frequency field operating, typically, at 27 or 40 MHz (Fig. 1.1). The sample, usually in liquid form, is introduced to the high temperature plasma (Fig. 1.2) as an aerosol mist (via pneumatic nebulization) and the particles

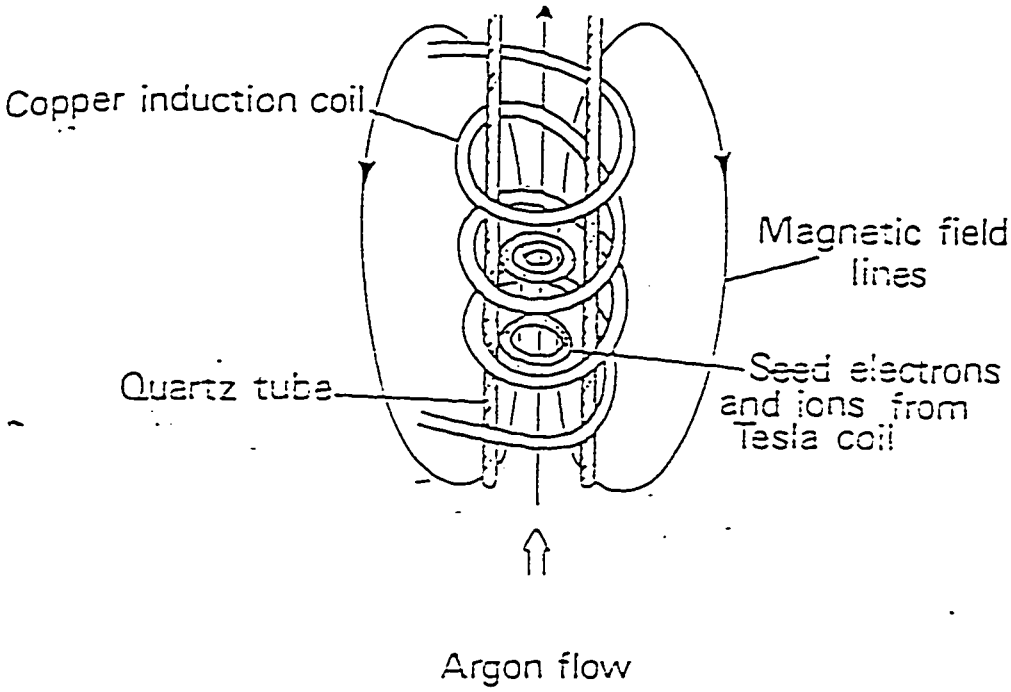


Fig. 1.1 Induced electric and magnetic field in the ICP.

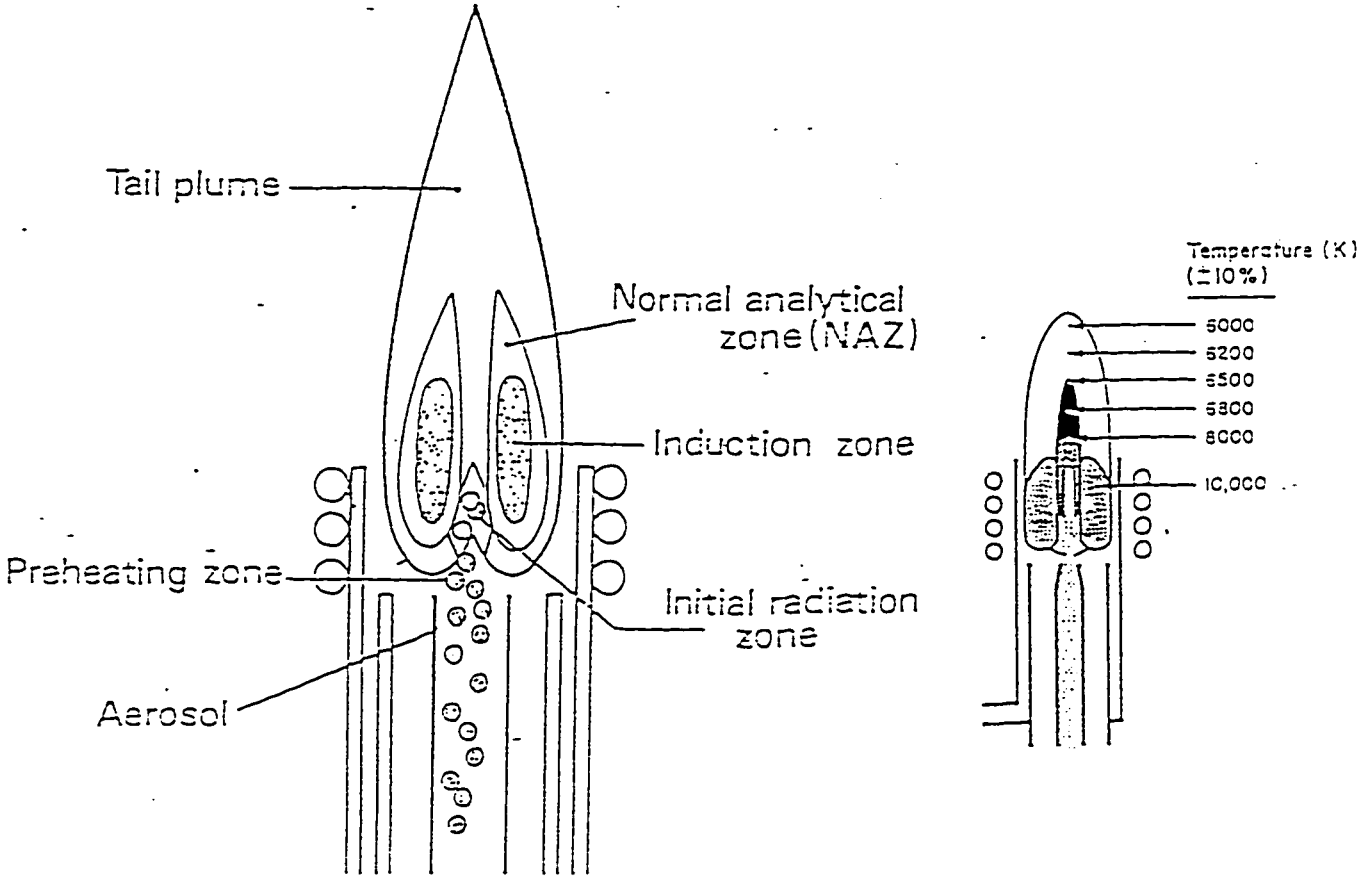


Fig. 1.2 Plasma geometry and vertical temperature profile.

undergo various processes such as desolvation, decomposition, atomization/excitation and ionization/excitation (Fig. 1.3). Once the atoms or ions are in their excited states, they can decay to lower states through thermal or radiative (emission) energy transition. The atomic and ionic emission, characteristic of analyte element, is received by a spectrometer and the multi-element emission signals are processed by a dedicated computer. A representation of the layout of a typical ICP-AES instrument[37] is shown in Figs. 1.4 & 1.5.

1.6 Internal Standard, Sample Introduction.

In selecting a sample introduction method for ICP-AES, the analyst should generally consider the requirements for sensitivity, stability, speed, sample size, sample type, corrosion resistance, and resistance to clogging. Cost and ease of use may also be of consideration. For most samples, a cross-flow nebulizer combined with a corrosion-resistance spray chamber and torch offers the best compromise for the above requirements[36].

In certain cases, the differences in the matrices of the standards and the sample are great enough to cause the sample introduction efficiencies for the standards and the sample to differ. Such differences in sample introduction efficiency represent an

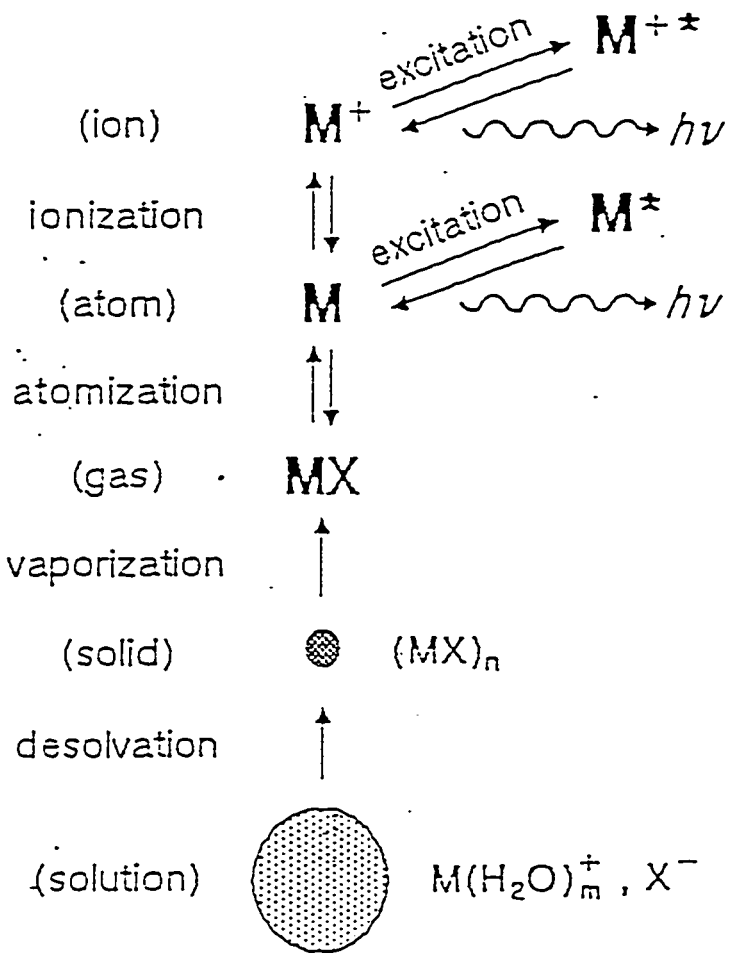


Fig. 1.3 The process of a sample introduction.

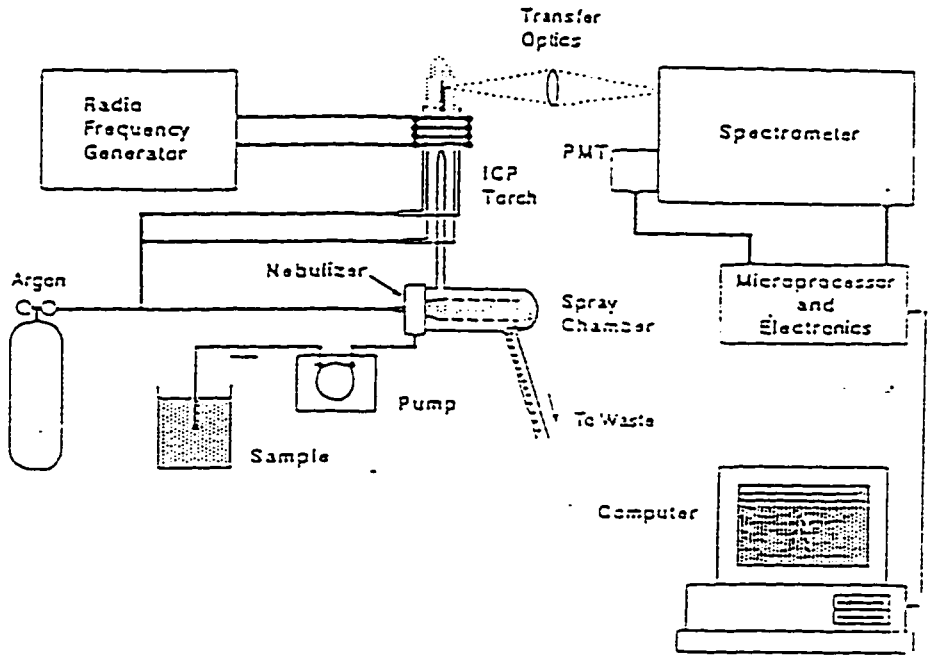


Fig. 1.4 Layout of typical ICP-AES

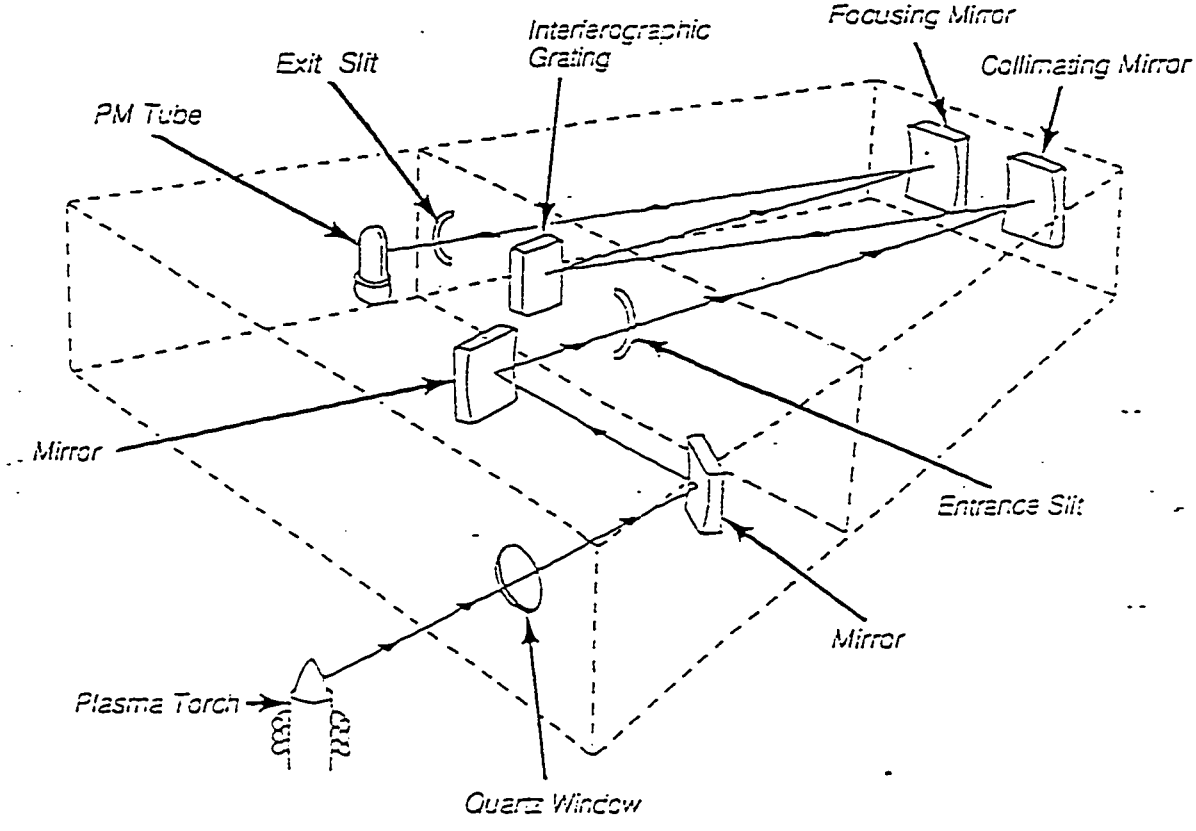


Fig 1.5 Plasma-400 optical schematic.

interference since an equal concentration of analyte in the standard and in the sample would not result in equivalent emission signal. These matrix interferences often originate from differences in surface tension and/or viscosity between the standards and the samples. The matrix interference most commonly encountered in ICP-AES results from high concentrations of dissolved solids in the sample solutions[36].

Special techniques may be required to obtain accurate results when a difficult matrix interference is present. One of the most popular techniques for correction of matrix interference is internal standardization. In this techniques, an element known as the internal standard (or internal reference) is used to indicate the relative amount of sample that transported to the plasma. The internal standard is an element that is present at the same concentration in all solutions to be analyzed, that is, standards, blanks and samples. This element can either be one that is present as a part of the matrix for all the solutions or one that is added to the standards, blank and samples during sample preparation. In this latter case, the internal standard element must not be previously present in the samples at a detectable concentration. The emission signal from the internal standard is then used to correct mathematically for differences in sample introduction efficiencies. Alternatives to internal standardization may include matrix matching the standards, blank, and samples, diluting the samples, or using the method of standard addition[36].

1.7 Objectives of the Study

It is obvious from literature that there have been no serious studies concerning the applications of polyoxyalkylene as extracting reagents for rare earth elements. This extraction facilitates preconcentration of these metal ions from their matrices and this may be imperative when these metal ions are to be determined by most of the experimental methods. In this study, liquid-liquid extraction of some lanthanide metal ions namely europium (Eu^{3+}), praseodymium (Pr^{3+}), and erbium (Er^{3+}), was investigated. The extraction were carried out from a picrate aqueous phase into 1,2-dichloroethane or nitrobenzene organic phase containing one of the polyoxyalkylene extractants. Polyoxyalkylene used were polyethylene glycol (PEG-600), polypropylene glycol (PPG-1,025 and 2,000) and polybutadiene oxide (PBO-700). These polyoxyalkylene ligands form ion pairs with the metal ions selectively depending upon the size and charge of the metal ion in addition to the nature of the polyoxyalkylene ligand.

It was expected that the study would provide information concerning percent separation or extraction of the above-mentioned metal ions individually from the aqueous into organic phase. The study also provided information concerning the nature of complexes (stoichiometry and complexing affinity) formed between the metal ions and the polyoxyalkylene ligands.

The study in this work was concerned only with noncyclic polyethers dissolved in nitrobenzene or 1,2-dichloroethane. The stoichiometry of polyoxyalkylene with lanthanide (Pr^{3+}, Eu^{3+} and Er^{3+}) metal ions will be investigated. The efficiency of these ligands to extract the metal cations has been assessed by inductively coupled plasma atomic emission spectroscopy.

CHAPTER II

EXPERIMENTAL PROCEDURE

2.1 Apparatus

2.1.1 Inductively Coupled Plasma Spectrophotometer

A Perkin Elmer Plasma Spectrometer,Plasma 400, equipped with one 3600 and one 1800 groove mm^{-1} grating was used. The torch is equipped with a porcelain injector tube and the plasma was run at 1300 w power with 15l/min. plasma, 1.1l/min. auxiliary and 1l/min. nebulizer argon flow rates. A 1.8 ml $min.^{-1}$ pump rate and a 35-s delay rinse time were set. The spectra were measured at an observation height of 11 mm with an integration time of 100 ms and a photomultiplier voltage of 600 V. Three replicate measurements were made for each sample. For all lines the built-in auto-background correction software as described by Salit et al[37] was utilized.

2.1.2 Mechanical Shaker

The shaker used (Burrel model 75) can accept 8 flasks up to 500 ml capacity. The metal case is mounted on four rubber feet, to absorb vibration. The built-in timer covers 0 to 60 minutes and has off and on manual override position. The electronic speed control is stepless. Supplied complete with side arms, 8 clamps and allen key. This mechanical shaker has been extensively used to mix two phases together (organic & aqueous).

2.1.3 pH Measurement

An Orion model 720 pH meter in conjunction with a corning combination glass electrode was used to measure the acidity of the aqueous solution. A typical cell for pH measurements with glass electrode is:

Ag, $AgCl_{(s)}$, 0.1N HCl II glass II test sample I satd.KCl, $Hg_2Cl_{2(s)}$, Hg

2.2 Chemicals Required and Preparations

A. Distilled water was passed through Ultrapure DI Cartridge [Fisher Scientific] to obtain deionized water which was used throughout the whole work.

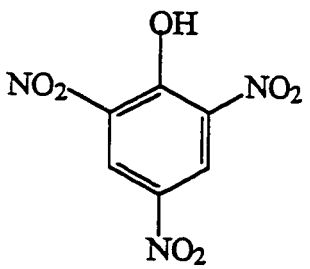
B. Concentrated HCl and HNO_3 (analytical grade, made by J. T. Baker).

HCl density = 1.191 δ/ml

HNO_3 = 1.424 δ/ml

different concentrations were prepared by pipeting certain volumes of the acid into volumetric flasks and diluting it using deionized water.

C. Picric acid (Analytical grade, Fluka).



Picric acid was dissolved in de-ionized water and standardized by 0.10M NaOH using phenolphthalein as an indicator. Various concentrations were prepared throughout the experiments.

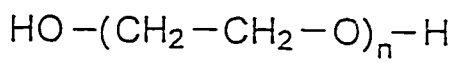
D. Stock standard solutions of europium, praseodymium, and erbium of 1000 ppm (Alfa Products) were used to prepare the working standards necessary to construct the working calibration curves. Other stock solutions were prepared from high-purity oxides 99.99% (made by Fluka). These oxides were dissolved in 10-30 ml of 6-9 M HCl and diluted to the final volume of 100 ml in a volumetric flask, giving a final concentration of 5,000 mg/L. The actual concentrations of these solutions were

checked by using the calibration curves obtained from Varian standard solutions.

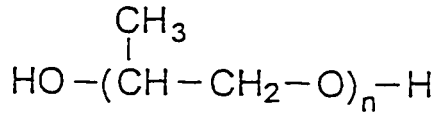
E. Nitrobenzene and 1,2-dichloroethane of analytical grade wre obtained from Fluka.

F. Polyoxyalkylenes were all provided by polyscience:

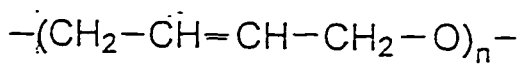
1- Polyethylene glycol (PEG-600)



2- Polypropylene glycol (PPG-1025 or 2000)



3- Polybutadiene oxide (PBO-700)



2.3 Table Curve Fitting Software

Table Curve Fitting Software (developed by Jandel Scientific) was used extensively to manipulate the data. This software is a specialized program that uses

automated statistical methods to process an X-Y data table for the best possible curve-fit equations. Once an appropriate equation has been selected , table curve can produce printed reports, files for use with major spreadsheet, scientific graphing, and presentation.

2.4 Extraction Procedure

The aqueous phase was prepared by mixing appropriate volumes of both , picric acid and metal ion solutions. The concentration of the metal ion was kept at around 100 mg/l. However, picric acid concentration was varied from 0.01 to 0.05M. The ligand of PEG, PPG or PBDO were dissolved in the organic solvent (nitrobenzene or 1,2-dichloroethane) to prepare concentration in the range of 0.1 to 0.5M.

Equal volumes (10 ml) of aqueous phase and organic phases were pipetted into 100 ml separatory funnel and shaken mechanically for 30 min. The mixture was left to stand for at least 30 min., so that the two layers were separated. Due the difference in the density of the two phases, the organic layer remained at the bottom of the separatory funnel. The aqueous phase was analyzed for the metal ion concentration using ICPAES. For analysis purposes, the aqueous phase was separated and diluted with deionized water and 10 ppm lanthanum (La^{+3}) was added as an internal standard.

The metal ion analysis in the organic phase was measured after stripping by 0.1M nitric or hydrochloric acid. The stripped metal ion concentration shows that the amount of metal ion lost from aqueous phase has been transferred completely to the organic phase. Thus, there was no need for further analysis in the organic phase.

2.5 Constructing the Working Calibration Curve

The analytical lines selected for analysis are presented in Table 2.1.

Table 2.1 The analytical line used for analysis.

Element	λ/nm
La	333.749
Pr	422.535
Eu	381.967
Er	369.265

The calibration curve for each metal ion was constructed from series of standard and blank solution. The sample solution was measured subsequently in triplicate. After measurement of all samples, the high reference solution was measured again as a check for all possible drift. Figures 2.1 to 2.3 show typical calibration

curves for praseodymium, europium and erbium. The correlation coefficient for all of these curves was better than 0.9999.

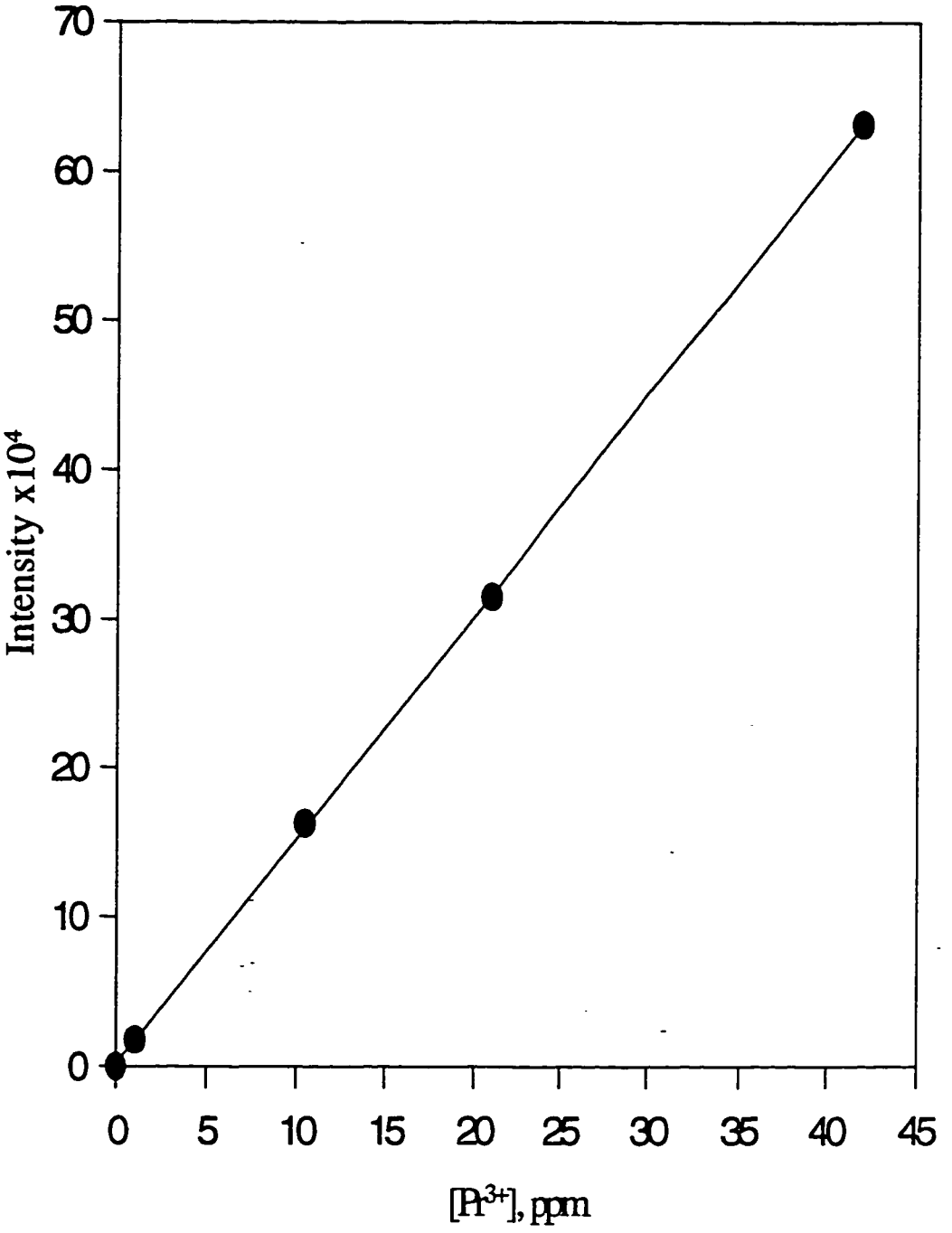


Fig. 2.1 Calibration curve for Pr^{3+}.

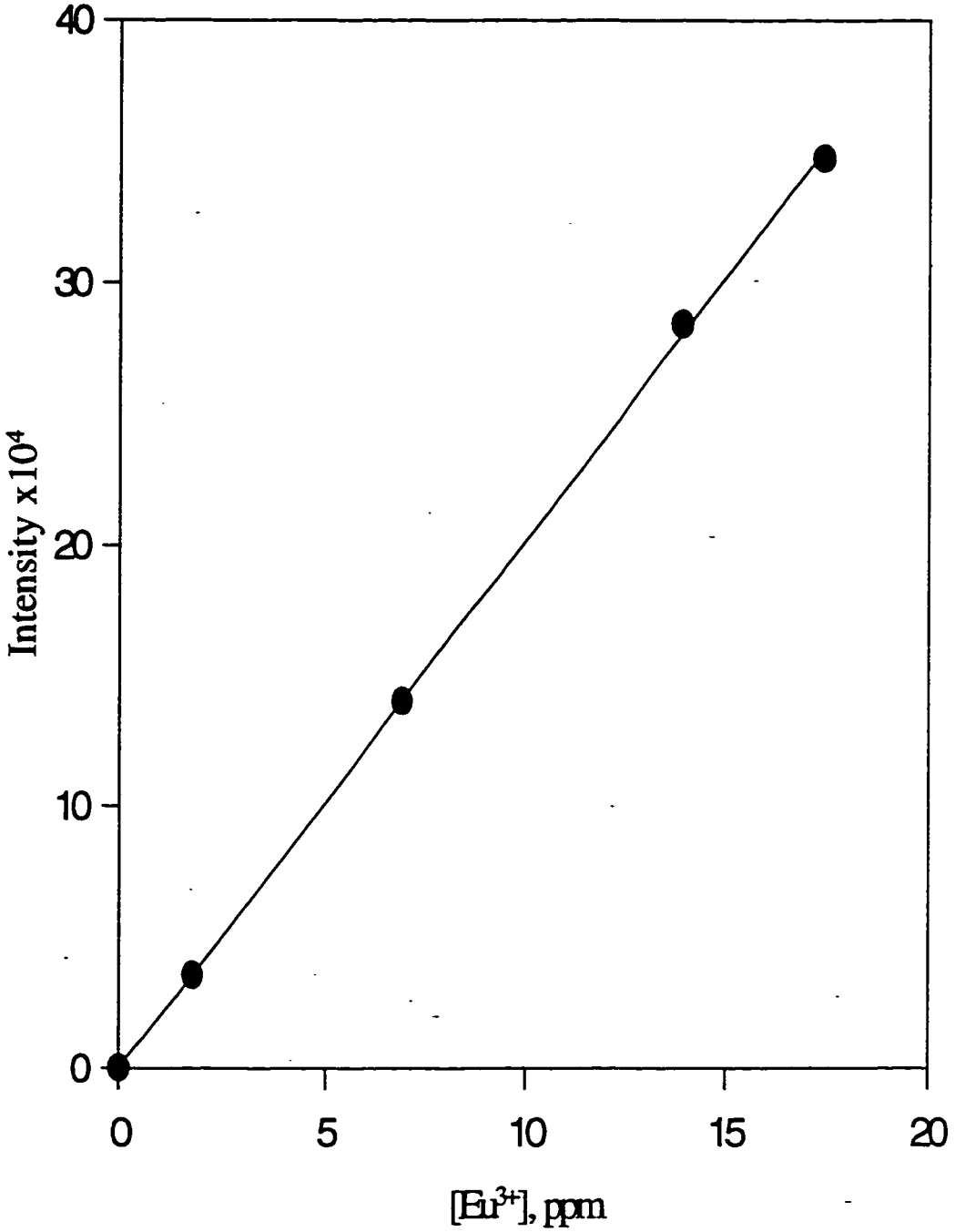


Fig. 2.2 Calibration curve for Eu^{3+}.

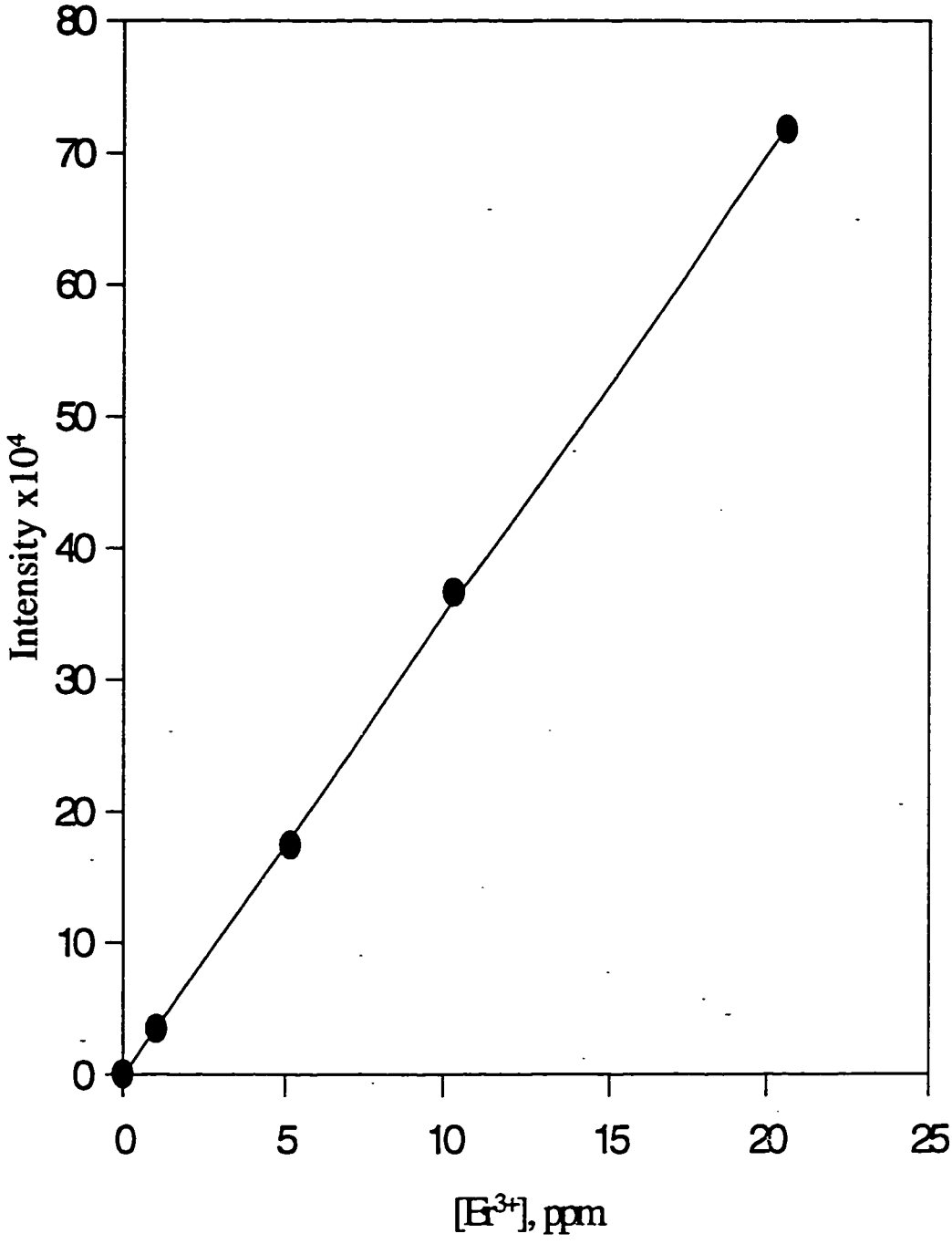


Fig. 2.3 Calibration curve for Er^{3+}.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Preliminary Studies

Solvent extraction of europium was initially tested with various extractants, namely polyethylene glycol (PEG), polypropylene glycol (PPG), polybutadiene oxide (PBDO), polypropylene glycol 400 dimethylacrylate (PPG400DMA), polytetramethylene ether glycol (PTMEG), and 18 crown 6 (18C6), as well as di-(2-ethylhexyl phosphate) in both nitrobenzene and 1,2-dichloroethane. PPG400DMA did not dissolve in either nitrobenzene or 1,2-dichloroethane. Thus, no further investigations were made with this ligand. 10 ml of aqueous solution containing 100 ppm Eu and 0.035 M picric acid was shaken with 10 ml of an organic phase containing a certain concentration of each of the above mentioned ligands. The results showed that the percent extraction in the case of di-(2- ethylhexyl phosphate) was 100% in both solvents.

The possibility of determining europium by ICP in the organic phase was investigated. Unfortunately, in the ICP instrument used for this work, the plasma (provided by the Perkin Elmer 400 ICP) was not suitable for nebulizing the two

organic solvents used. The preliminary experiments showed that carbon builds up on the injector tube leading to a non-sustained plasma[38]. As a solution, europium was stripped out from the organic layer into an aqueous phase where it is easy to handle the analysis. In fact, after extraction of the europium (100 ppm) from picric acid (0.0480 M) into the organic phase with polypropylene glycol, for example, the organic phase was stripped with 10 ml of various stripping agents ranging from 0.1 to 5 M concentration of nitric acid and hydrochloric acid. Generally, 1 M nitric acid was preferred as the stripping agent since it was effective over a wide range of europium concentrations.

3.2 Variables Affecting the Solvent Extraction

Solvent extraction studies indicated that the amount of lanthanide metal ion extracted from the aqueous phase into an organic phase containing polyoxyalkylene nonionic surfactants is dependent upon various variables, namely, pH of the aqueous phase, concentration of picric acid in the aqueous phase, the organic solvent and nature of the polyoxyalkylene species. These variables have been extensively investigated to determine the optimum extraction conditions.

3.2.1 Effect of Nature and Concentrations of Ligand and the Organic Phase at Low pH

Lanthanide metal ions Eu^{3+}, Pr^{3+}, and Er^{3+}, were extracted from 0.05 M picric acid without pH adjustment (pH measurment was mostly << 2) by various concentrations of polyoxyalkylene (Tables 3.1 to 3.5) in nitrobenzene phase. The extraction was incomplete for all metals studied. Among the three metal ions studied, Pr^{3+} , showed the highest extraction efficiency (78%) with 0.3M PPG-1025 concentration (Table 3.2) in nitrobenzene phase. The extraction efficiency was 78% in the case of Pr^{3+} (Table 3.2), 72% in the case of Eu^{3+} (Table 3.1) and 52% in the case of Er^{3+} (Table 3.3). This decrease in percent extraction is consistent with the decrease in the ionic radii for the ions which are 1.013A° for Pr^{3+}, 0.950A° for Eu^{3+} and 0.881A° for Er^{3+}.

In fact, there is a competition between hydration and complexing efficiency since at least some of the water of hydration must be stripped from the cation to accommodate it within the oxygen cage provided by the polyoxyalkylene molecule. The high electric charge density of the smaller cations greatly attracts both water and oxygens from the polyoxyalkylene molecules. Thus, the tendency for hydration becomes greater for smaller cations.

Comparing the extractibility of europium ion by 0.3M of PPG-1,025, PEG-600 and PBDO-700 shows that PPG-1025 is the most efficient extractant. 72% of Eu^{3+} was extracted by PPG-1025 (Table 3.1), ~41% of Eu^{3+} was extracted by PEG-600 (Table 3.4) and 21% of Eu^{3+} was extracted by PBDO-700 (Table 3.5) into the nitrobenzene organic phase.

When the extraction of the three metal ions has been carried out using 1,2-dichloroethane rather than nitrobenzene, the same sequence of extraction efficiency towards the three metal ions has been observed considering the nature of the polyoxyalkylenes or the type of the metal ion extracted (Tables 3.6 to 3.10 and Figures 3.6 to 3.10). However, the extraction efficiencies in all cases studied were much less than the case of nitrobenzene organic diluent. Tables 3.6 to 3.8 and figures 3.6 to 3.8 indicate that the highest percent extraction achieved by PPG-1025 for Eu^{3+}, Pr^{3+},and Er^{3+} was 58.9%, 67.1%, and 39.5% compared to 72.5% , 78.6% , and 51.9% when nitrobenzene was the organic phase. Further more, the highest percent extraction Eu^{3+} with PPG-1025, PEG-600, and PBDO-700 was 58.9%, 14.0%, and 6.8% respectively (Tables 3.6, 3.9, and 3.10) compared to 72.5%, 41.0%, and 21.3% (Tables 3.1,3.4, and 3.5) in the case of nitrobenzene. A similar behavior has been reported previously by Adams et al.[40], where they studied the extraction of aurocyanide ion-pairs with alkali metal ions into organic phase containing long chain polyethers, namely Titon X-100. Adams, treated this matter extensively using all

Table 3.1 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations of PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
99.00	88.80	0.0082	11.20
99.00	73.46	0.0302	25.79
99.00	66.76	0.0486	32.56
99.00	45.23	0.1030	54.31
99.00	27.26	0.2933	72.46

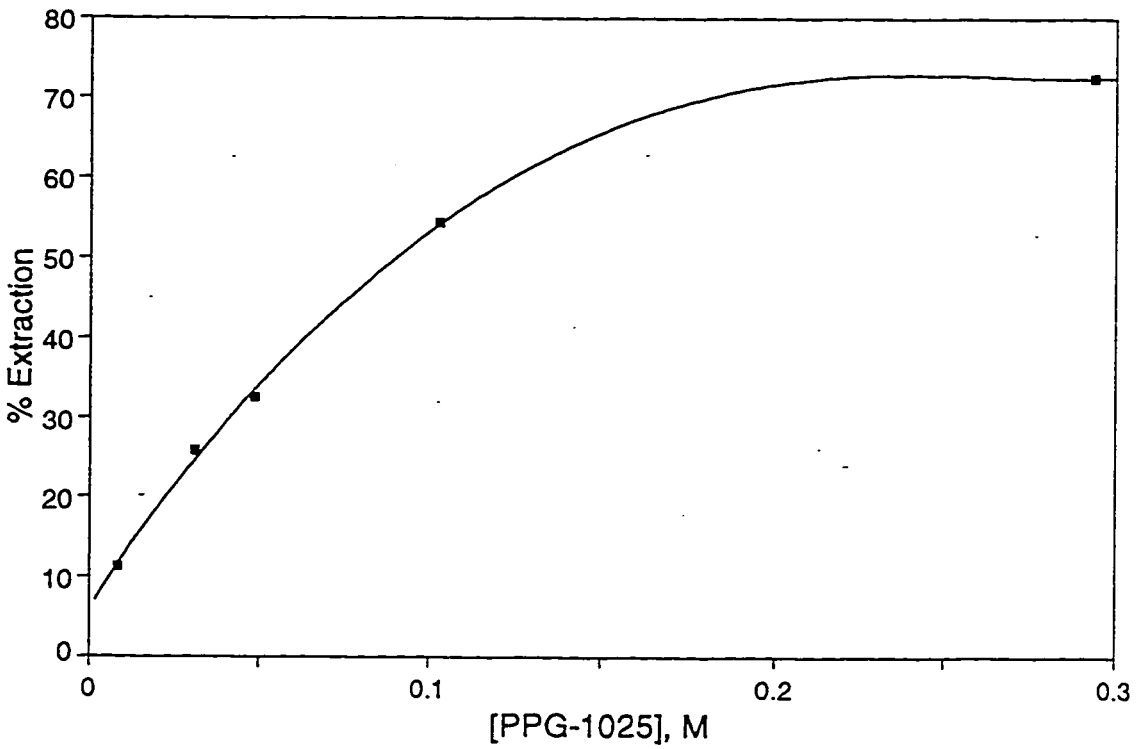


Fig. 3.1 Extraction of Eu^{3+} into nitrobenzene by PPG-1025

Table 3.2 Extraction of Pr^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations PPG-1025.

$[Pr^{3+}]$ before extraction, ppm	$[Pr^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
99.57	70.20	0.0206	29.50
99.57	56.82	0.0401	42.94
99.57	41.55	0.0945	58.27
99.57	26.60	0.2053	73.28
99.57	21.36	0.2936	78.55

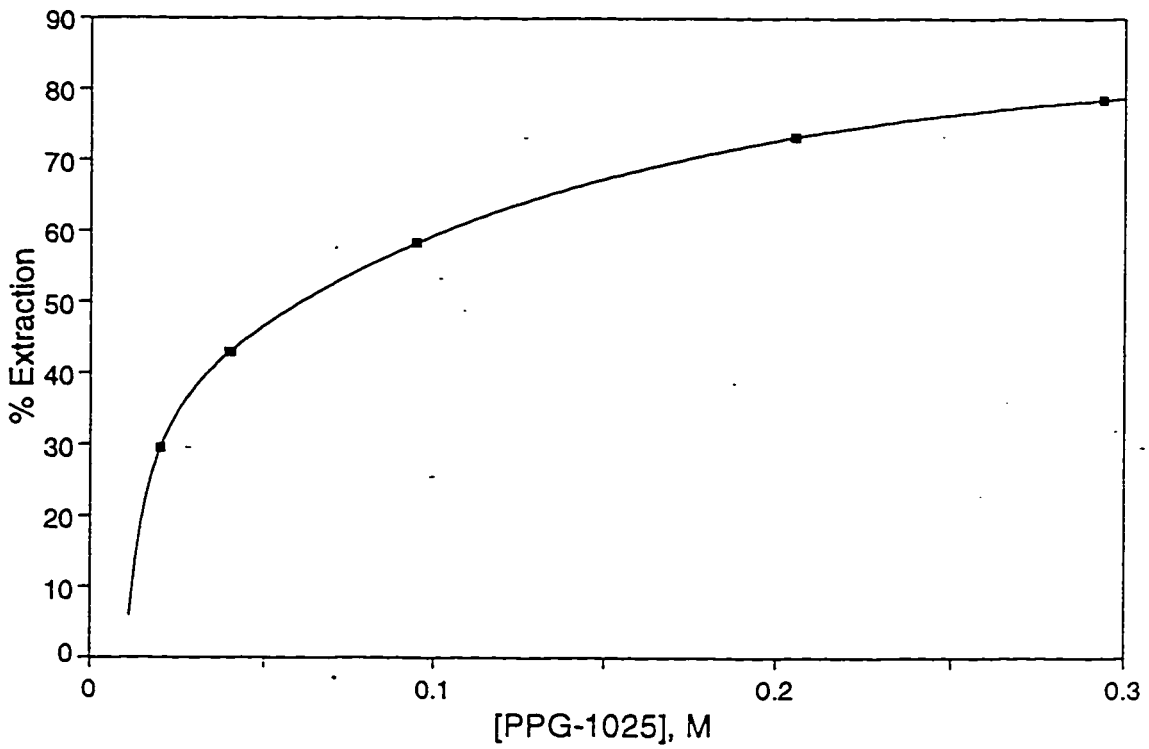


Fig. 3.2 Extraction of Pr^{3+} into nitrobenzene by PPG-1025

Table 3.3 Extraction of Er^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations PPG-1025.

$[Er^{3+}]$ before extraction, ppm	$[Er^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
101.00	94.17	0.0089	6.76
101.00	86.23	0.0304	14.62
101.00	80.02	0.0474	20.77
101.00	64.46	0.1198	36.18
101.00	48.58	0.2992	51.90

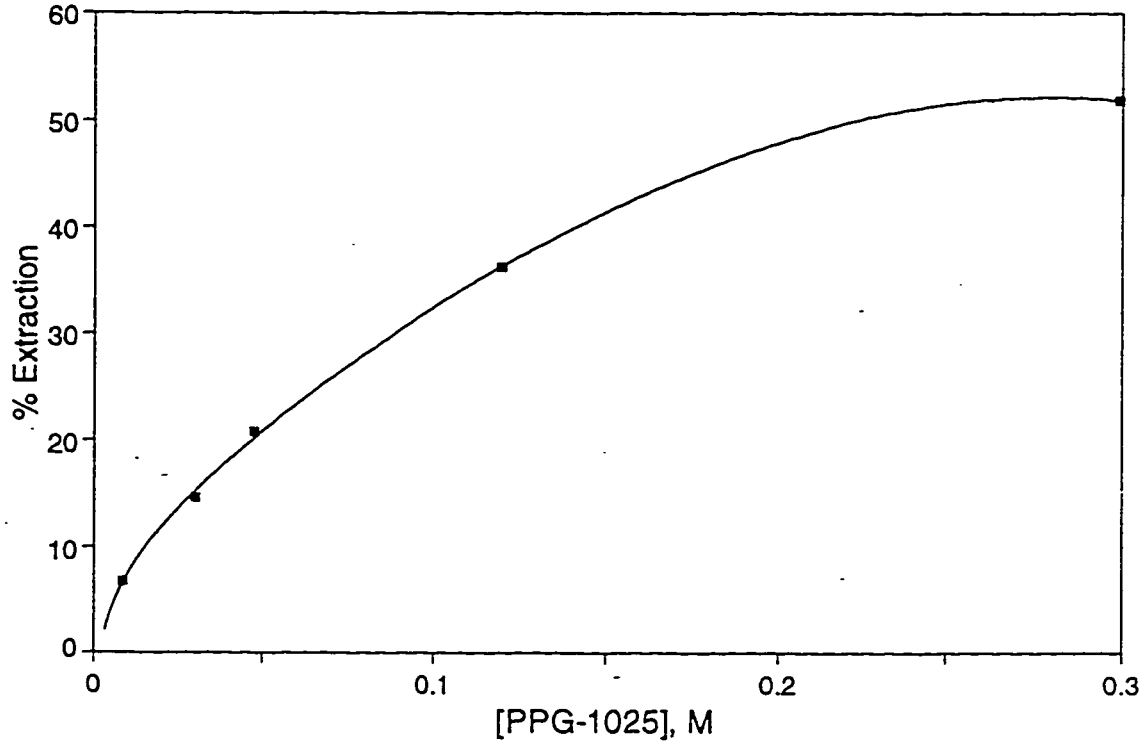


Fig. 3.3 Extraction of Er^{3+} into nitrobenzene by PPG-1025

Table 3.4 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations of PEG-600.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PEG-600], M	% Extraction
97.00	85.80	0.0212	11.55
97.00	79.18	0.0646	18.37
97.00	70.43	0.1076	27.39
97.00	60.08	0.2152	38.06
97.00	57.23	0.3000	41.00

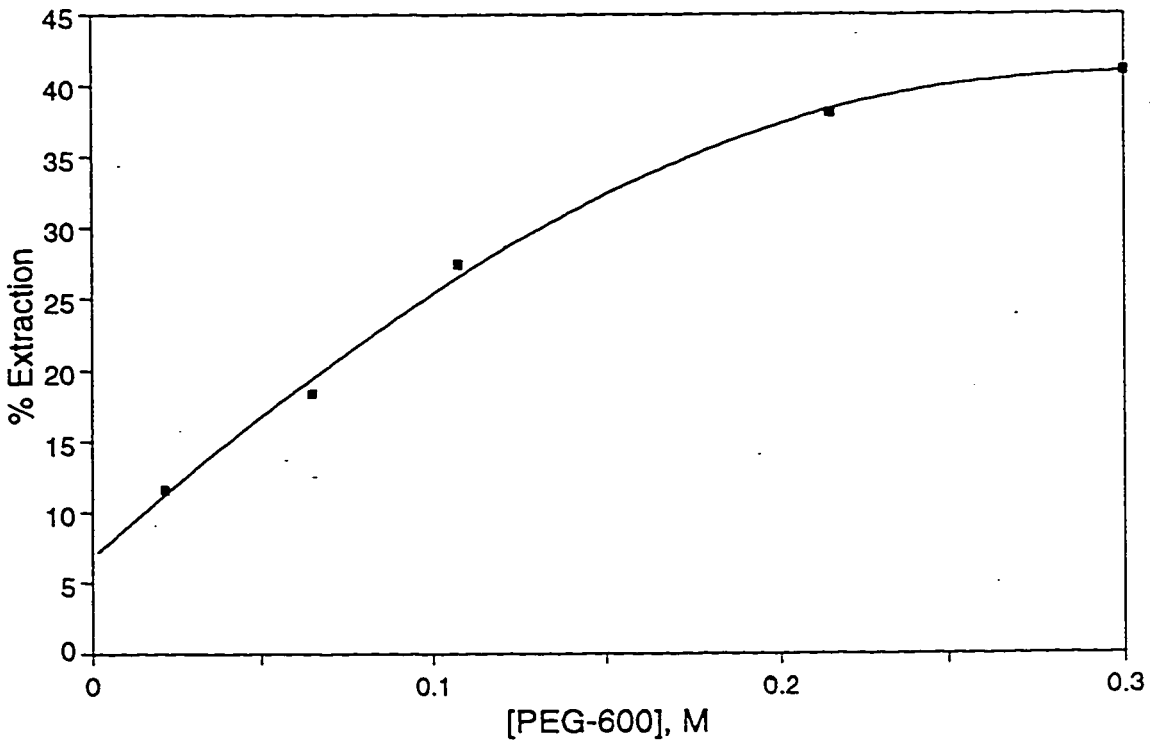


Fig. 3.4 Extraction of Eu^{3+} into nitrobenzene by PEG-600

Table 3.5 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations of PBDO-700.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PBDO-700], M	% Extraction
98.00	89.92	0.0113	8.25
98.00	82.04	0.0226	16.28
98.00	77.95	0.0338	20.46
98.00	77.73	0.1128	20.68
98.00	77.09	0.2921	21.34

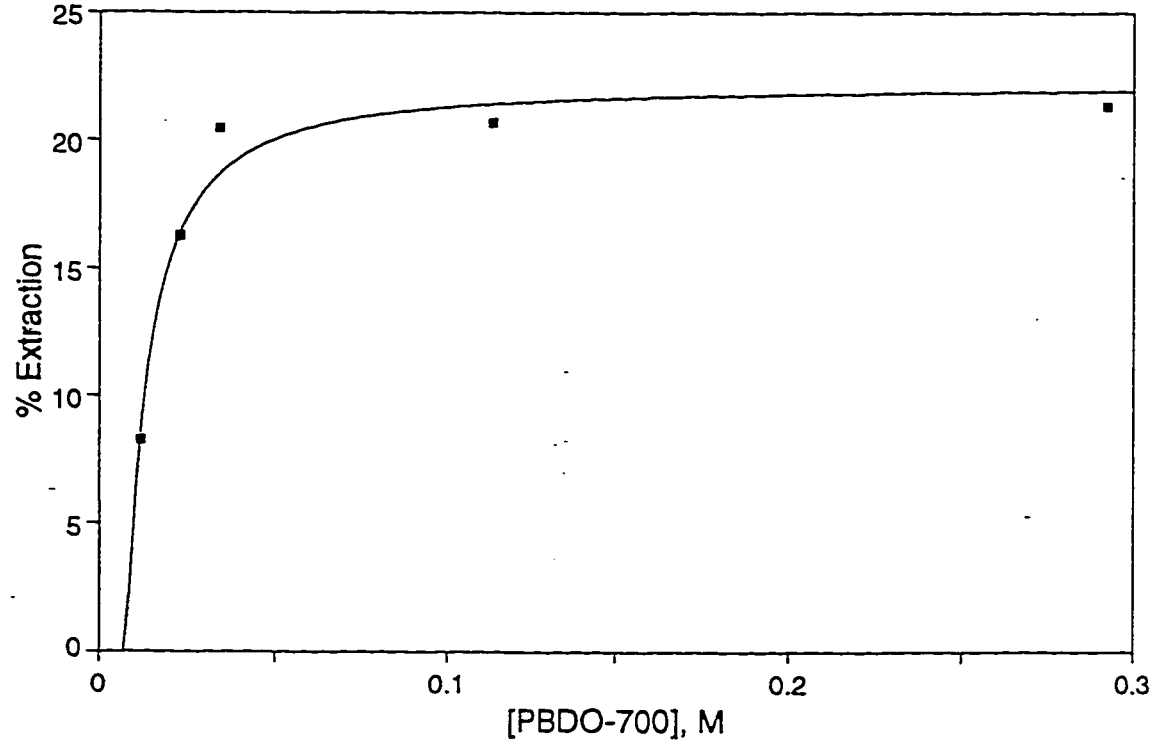


Fig. 3.5 Extraction of Eu^{3+} into nitrobenzene by PBDO-700

the available literature reports and some molecular mechanics calculations. They ascribed this behavior to the difference in the dielectric constant of the organic solvents which is significantly high for nitrobenzene. They attributed the superiority of extraction into the nitrobenzene phase to the great energy of solvation of the lipophilic anion by high polar solvent compared to the solvent of low polarity. They also adopted the ion-pair model in the previous literature reports in which the polyether is coordinated to the metal ion through ether oxygen atoms of the polyether which wraps around the cation in a helical configuration, a conformation stabilizes more by high dielectric constant solvents. They suggested that uncomplexed polyether is almost linear in a low dielectric constant solvent. However, a linear helical conformation is highly preferred in solvents of high dielectric constants. As a result of their molecular mechanics model, they suggested that the complexed polyether in either low or high dielectric constant solvent should be in the helical conformation. Consequently, polyethers in the low dielectric constant solvents must show a modification in conformation from linear to the helical form before complexation with the metal ions takes place. Thus, the complexation is more favorable in the high dielectric constant solvents in which the polyethers are already in a helical conformation.

Table 3.6 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations of PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
99.00	98.40	0.0084	0.60
99.00	94.21	0.0276	4.84
99.00	88.76	0.0466	10.34
99.00	71.70	0.1028	27.58
99.00	40.67	0.3015	58.92

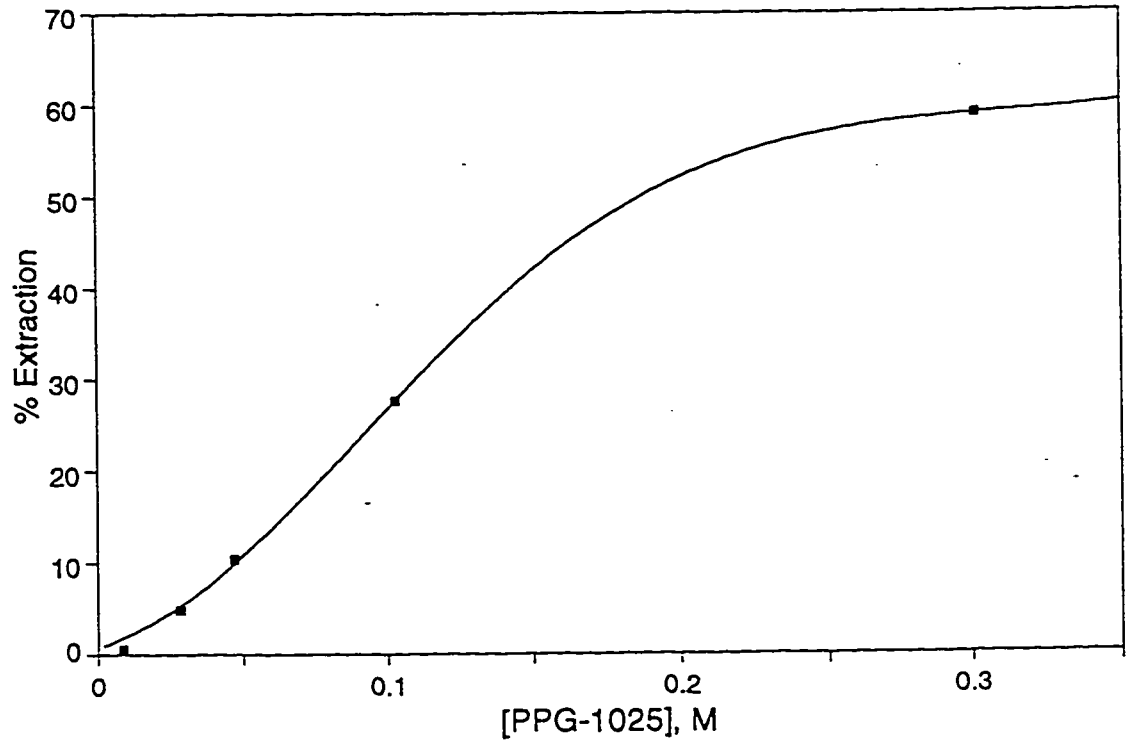


Fig. 3.6 Extraction of Eu^{3+} into 1,2-dichloroethane by PPG-1025

Table 3.7 Extraction of Pr^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations of PPG-1025.

$[Pr^{3+}]$ before extraction, ppm	$[Pr^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
99.57	84.74	0.0202	14.89
99.57	77.54	0.0406	22.12
99.57	59.73	0.0986	40.01
99.57	40.93	0.2058	58.89
99.57	32.75	0.2936	67.11

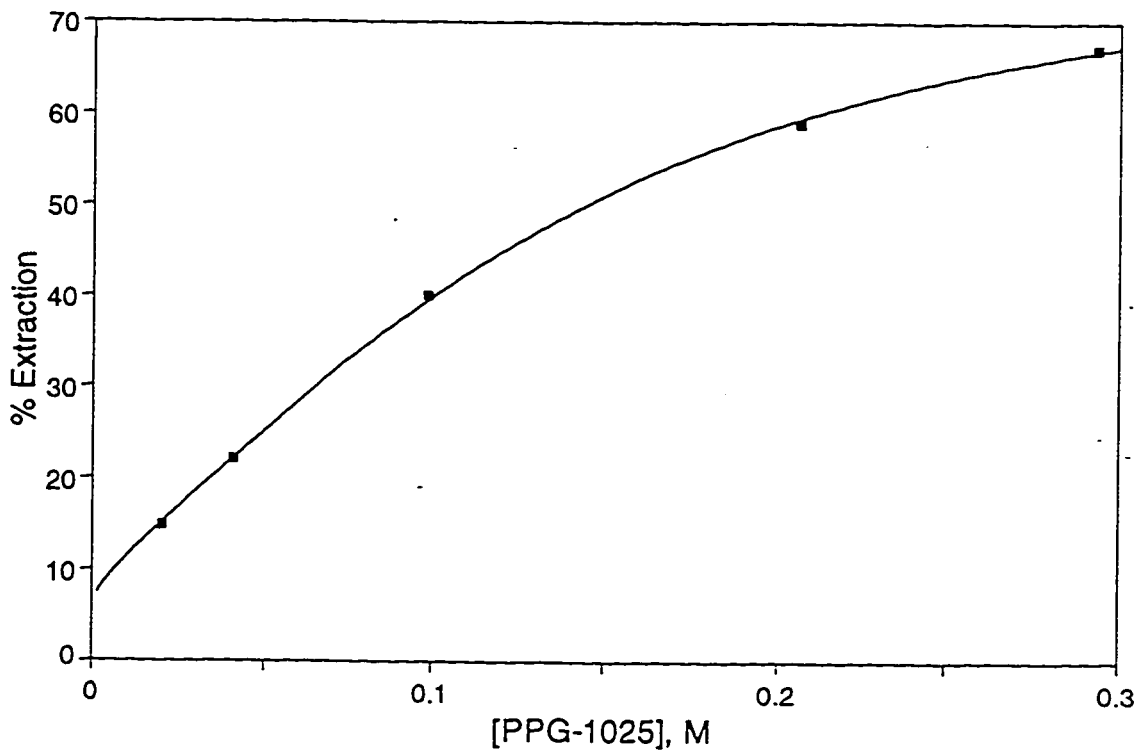


Fig. 3.7 Extraction of Pr^{3+} into 1,2-dichloroethane byPPG-1025

Table 3.8 Extraction of Er^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations of PPG-1025.

$[Er^{3+}]$ before extraction, ppm	$[Er^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
101.00	98.95	0.0087	2.03
101.00	94.35	0.0306	6.58
101.00	90.81	0.0493	10.09
101.00	79.50	0.1215	21.29
101.00	61.06	0.3003	39.54

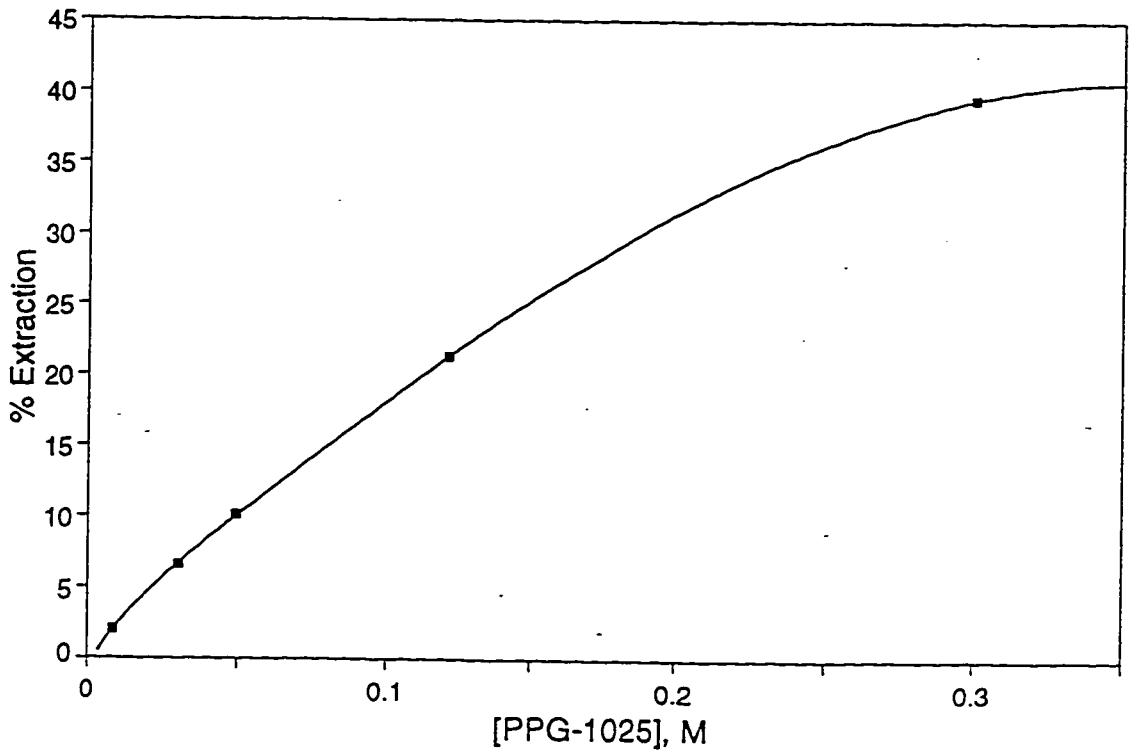


Fig. 3.8 Extraction of Er^{3+} into 1,2-dichloroethane by PPG-1025

Table 3.9 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations of PEG-600.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PEG-600], M	% Extraction
97.00	95.06	0.0218	2.00
97.00	90.81	0.0655	6.38
97.00	87.82	0.1092	9.46
97.00	86.01	0.2184	11.33
97.00	83.42	0.3003	14.00

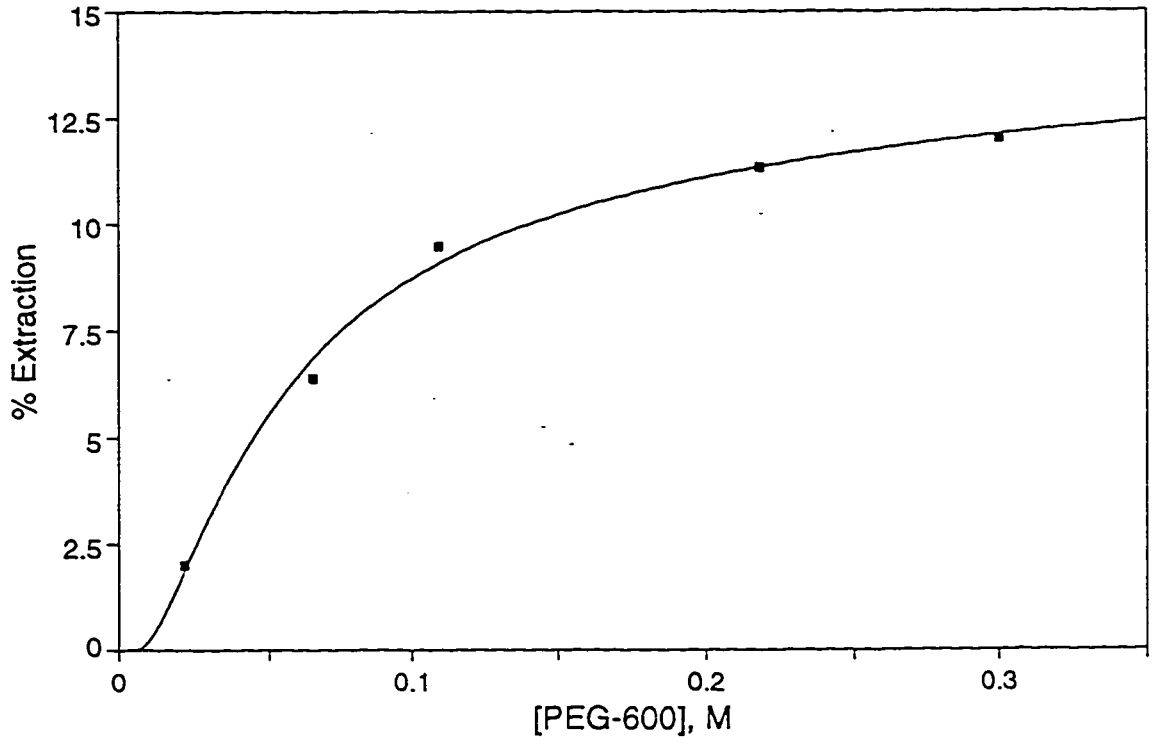


Fig. 3.9 Extraction of Eu^{3+} into 1,2-dichloroethane by PEG-600

Table 3.10 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations PBDO-700.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PBDO-700], M	% Extraction
98.00	94.23	0.0115	3.85
98.00	91.63	0.0230	6.50
98.00	91.98	0.0345	6.14
98.00	91.43	0.1150	6.70
98.00	91.32	0.3003	6.82

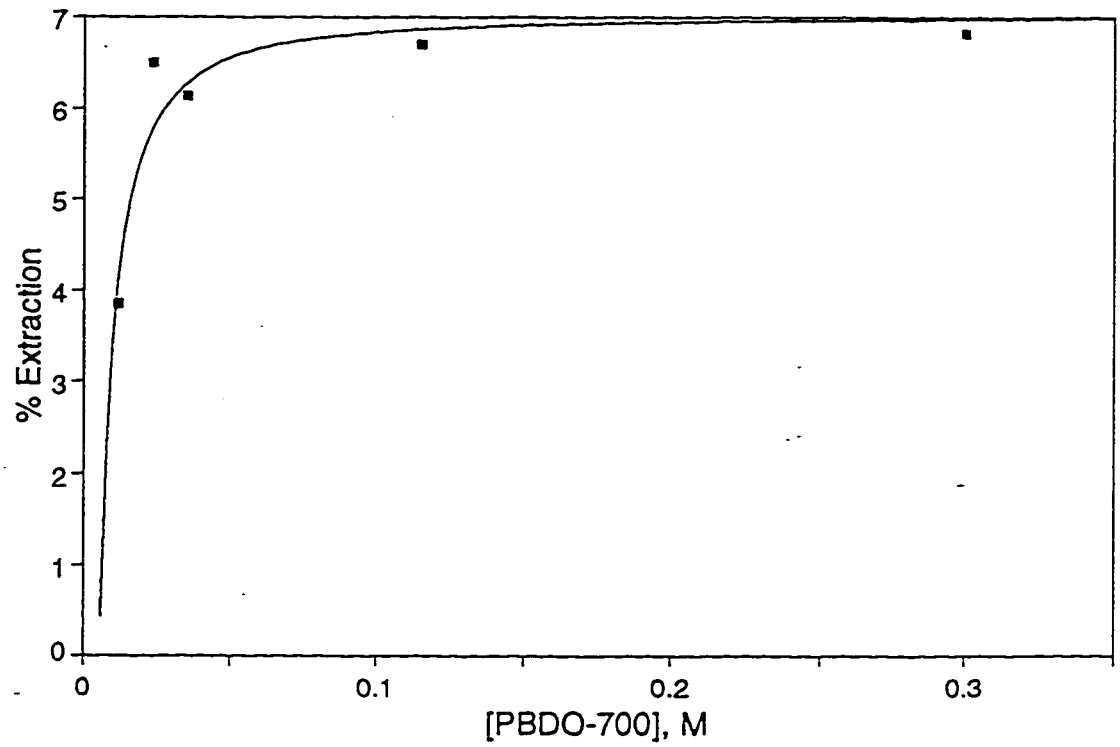


Fig. 3.10 Extraction of Eu^{3+} into 1,2-dichloroethane by PBDO-700

3.2.2 Effect of Picric Acid Concentration on Extraction Efficiency

Since the lipophilic picrate anion plays an important role in the metal ion extraction process, the extraction has been tested at various picric acid concentrations starting from about $1x10^{-2}$ M up to about $5.5x10^{-2}$ M. However, the maximum picrate concentration was limited by its solubility. The initial concentration of metal ions was kept at a constant level of about 100 ppm and the polyoxyalkylene nonionic surfactant was kept at a level of about 0.1M.

Tables 3.11 to 3.20 and Figures 3.11 to 3.20 show an increase in the percent extraction of the three metal ions studied using PPG-1025, PEG-600 or PBDO-700 in a nitrobenzene or dichloroethane phase. However, the percent extraction of all metal ions studied was significantly low even in the presence of 5.5×10^{-3} M picric acid. This behavior may be attributed to the competition between the proton and the lanthanide metal ion to form ion-pair with the picrate anion which will be finally extracted the organic phase. The percent extraction of these metal ions increases with the concentration of picric acid, however, the extraction was limited by the acidity of medium.

The possibility of extracting picric acid as HPic from its aqueous solution into nitrobenzene phase was studied. It has been reported by Rais and Selucky[41], that at

Table 3.11 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1025M PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
99.00	90.52	10.67	8.56
99.00	80.18	21.35	19.04
99.00	68.31	32.02	31.00
99.00	55.46	40.56	43.98
99.00	47.06	52.17	52.46

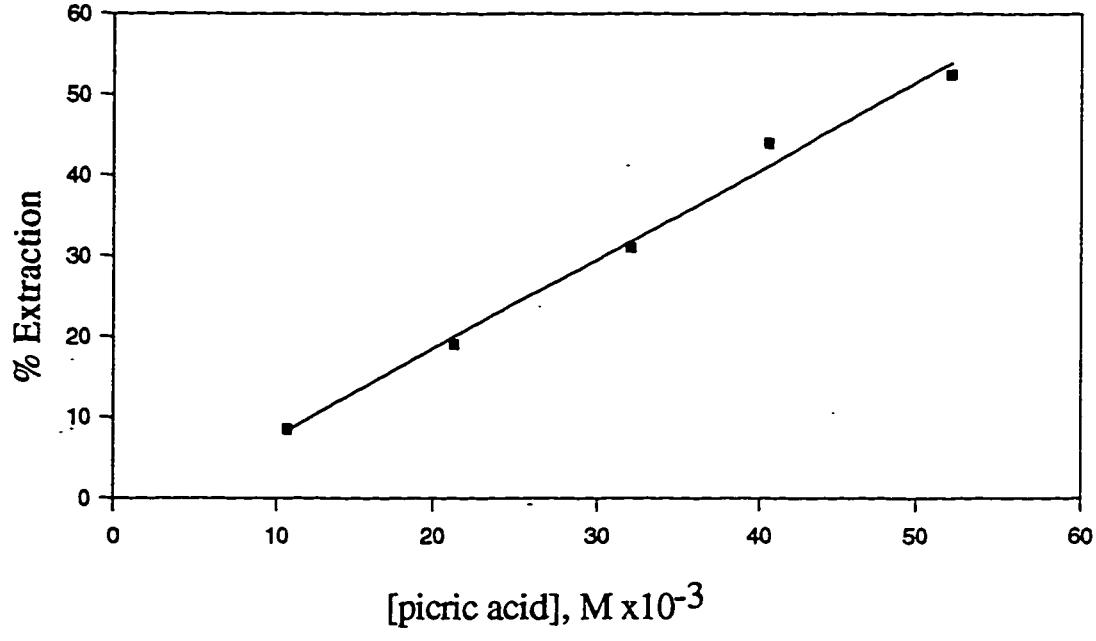


Fig. 3.11 Extraction of Eu^{3+} into nitrobenzene by PPG-1025 at various picrate concentrations.

Table 3.12 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1025M PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
99.00	95.97	10.67	3.06
99.00	90.04	21.35	9.05
99.00	82.57	32.02	16.59
99.00	76.05	40.56	23.18
99.00	67.91	52.17	31.40

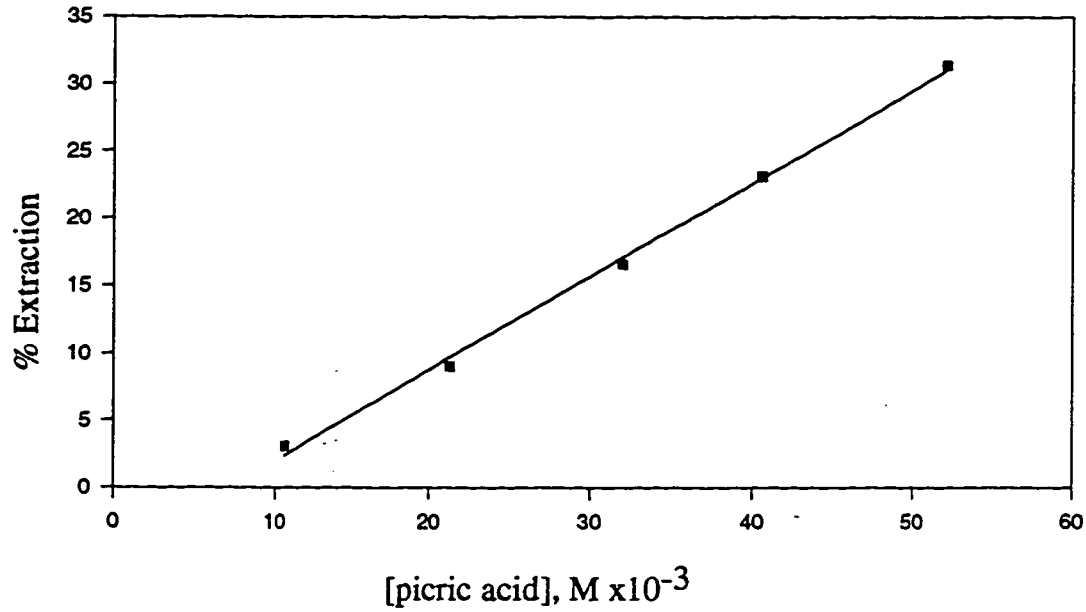


Fig. 3.12 Extraction of Eu^{3+} into 1,2-dichloroethane by PPG-1025 at various picrate concentrations.

Table 3.13 Extraction of Pr^{3+} from aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1030M PPG-1025.

$[Pr^{3+}]$ before extraction, ppm	$[Pr^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
99.57	90.97	11.38	8.64
99.57	79.12	22.76	20.54
99.57	58.46	34.14	41.29
99.57	47.95	45.52	51.84
99.57	41.88	52.35	57.94

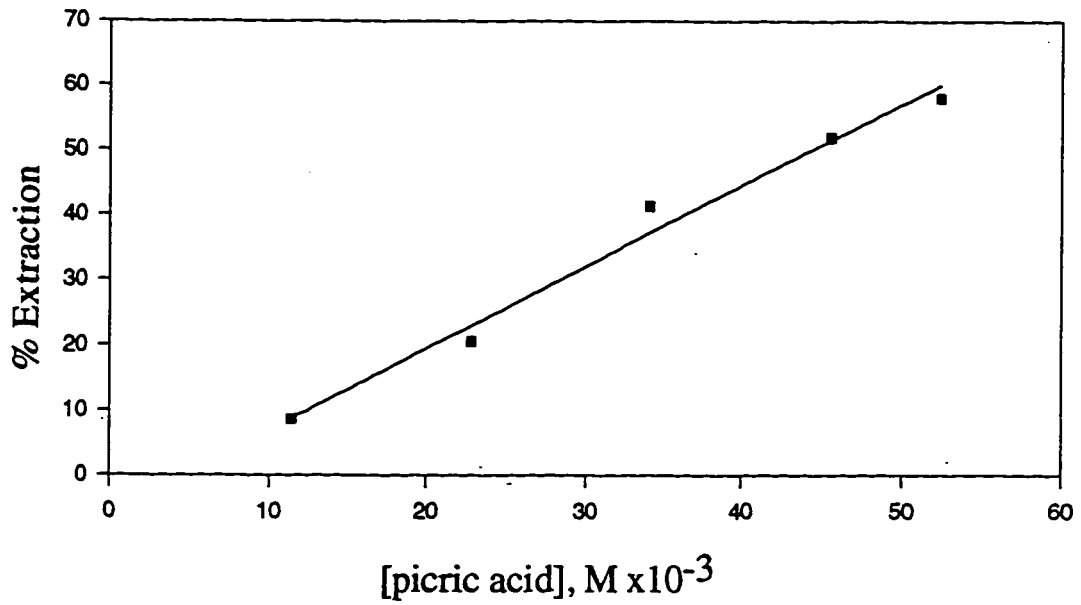


Fig. 3.13 Extraction of Pr^{3+} into nitrobenzene by PPG-1025 at various picrate concentrations.

Table 3.14 Extraction of Pr^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1028M PPG-1025.

$[Pr^{3+}]$ before extraction, ppm	$[Pr^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
99.57	93.55	11.38	6.05
99.57	85.24	22.76	14.39
99.57	77.42	34.14	22.24
99.57	69.56	45.52	30.14
99.57	65.67	52.35	34.05

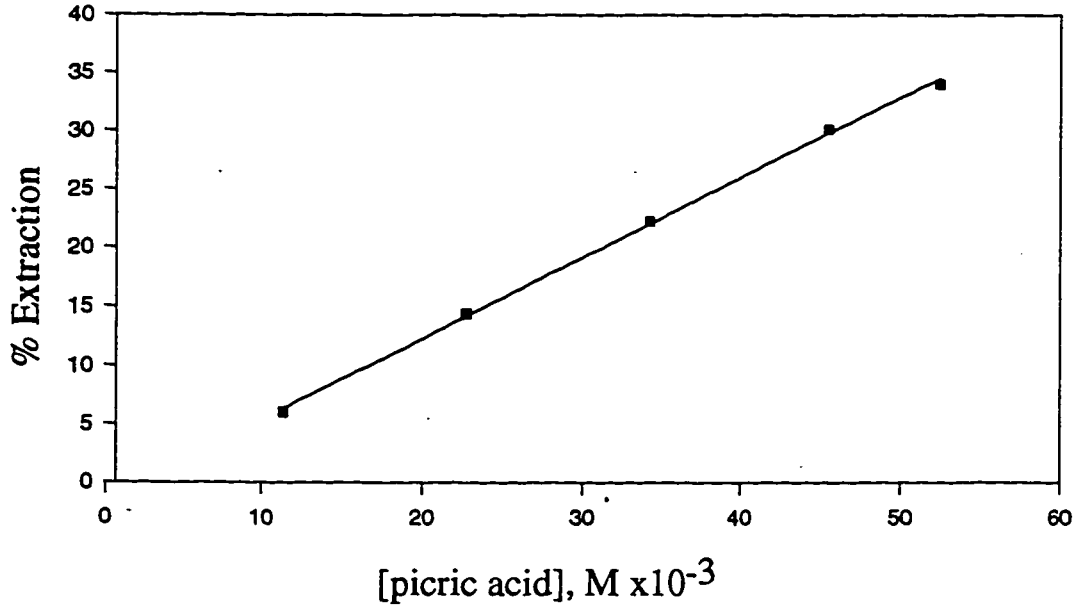


Fig. 3.14 Extraction of Pr^{3+} into 1,2-dichloroethane by PPG-1025 at various picrate concentrations.

Table 3.15 Extraction of Er^{3+} from an aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1198M PPG-1025.

$[Er^{3+}]$ before extraction, ppm	$[Er^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
101.00	91.82	11.40	9.09
101.00	76.76	22.80	24.00
101.00	63.43	34.10	37.20
101.00	52.52	45.50	48.00
101.00	45.45	54.60	55.00

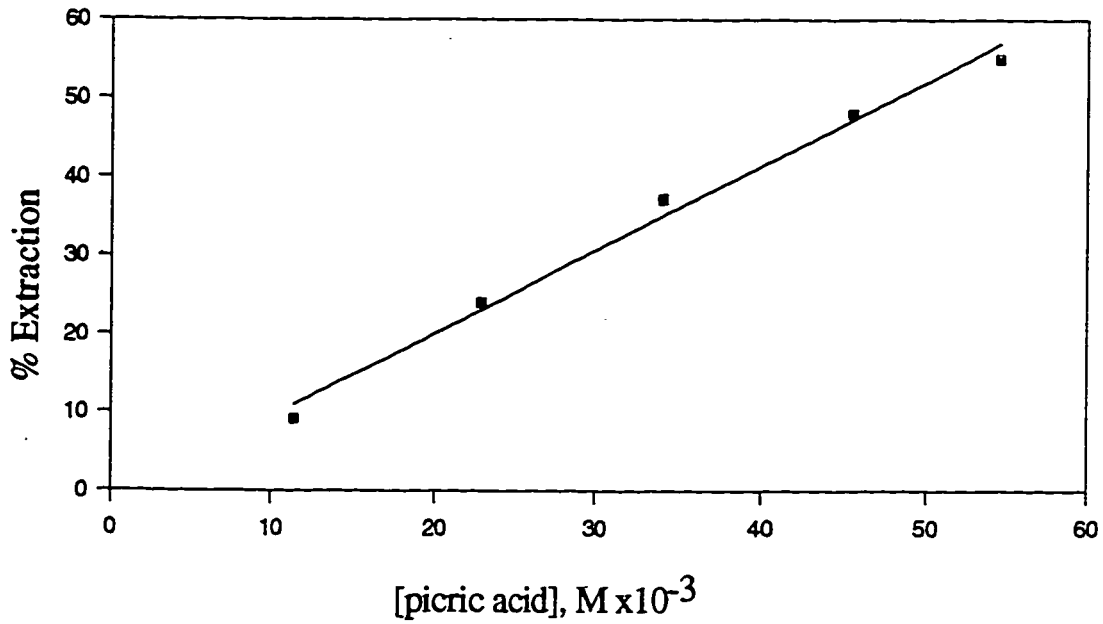


Fig. 3.15 Extraction of Er^{3+} into nitrobenzene by PPG-1025 at various picrate concentrations.

Table 3.16 Extraction of Er^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1215M PPG-1025.

$[Er^{3+}]$ before extraction, ppm	$[Er^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
101.00	95.00	11.40	5.94
101.00	85.65	22.80	15.20
101.00	76.76	34.10	24.00
101.00	67.77	45.50	32.90
101.00	61.61	54.60	39.00

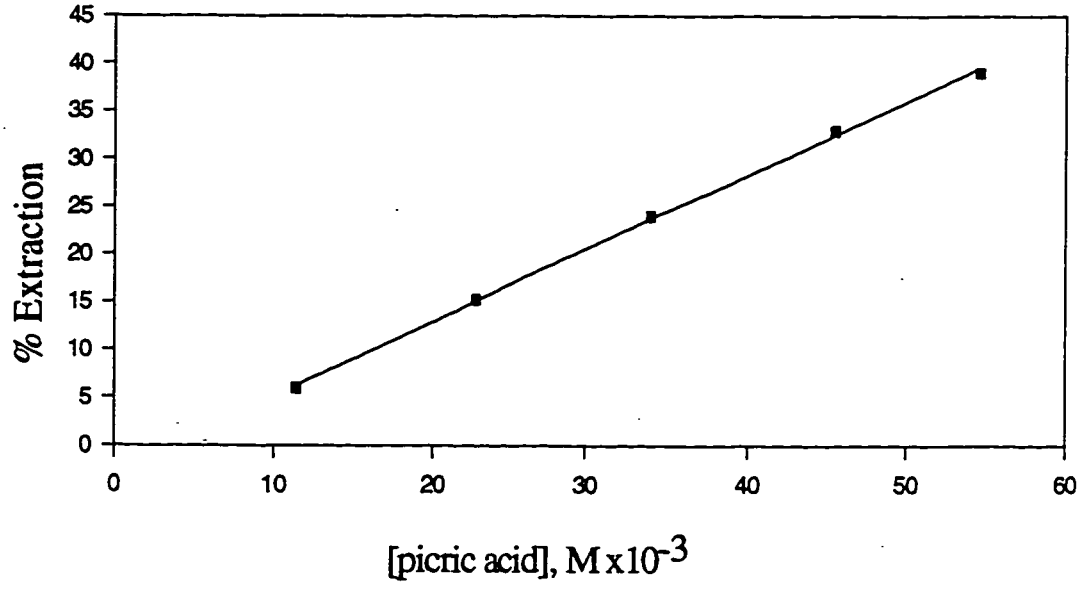


Fig. 3.16 Extraction of Er^{3+} into 1,2-dichloroethane by PPG-1025 at various picrate concentrations.

Table 3.17 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1125M PEG-600.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
97.00	90.72	11.38	6.47
97.00	80.77	22.76	16.73
97.00	69.38	34.14	28.47
97.00	60.24	45.52	37.90
97.00	53.50	54.62	44.84

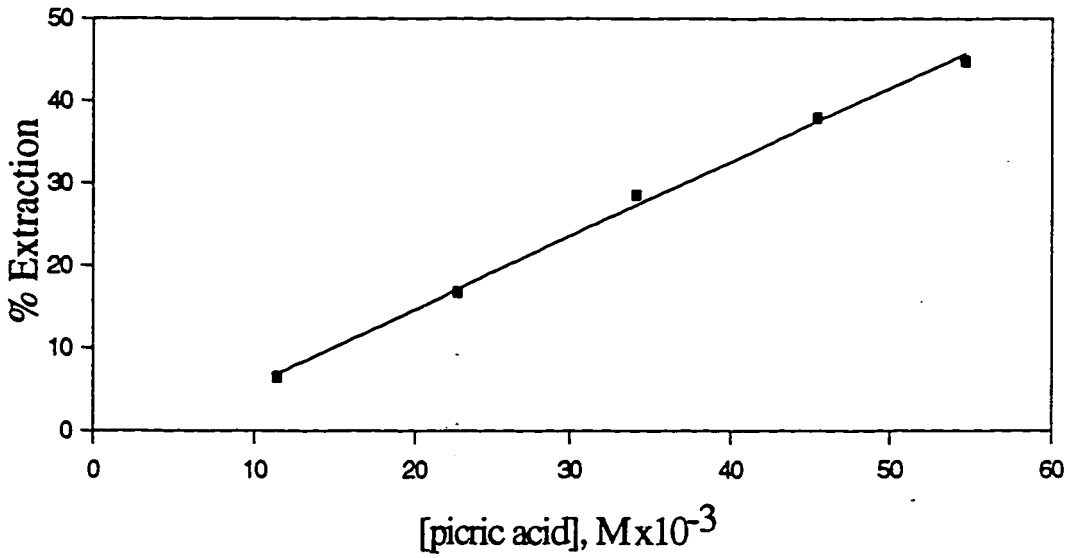


Fig. 3.17 Extraction of Eu^{3+} into nitrobenzene by PEG-600 at various picrate concentrations.

Table 3.18 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1035M PEG-600.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
97.00	89.86	11.38	7.36
97.00	83.73	22.76	13.68
97.00	72.45	34.14	25.31
97.00	62.56	45.52	35.50
97.00	59.94	54.62	38.21

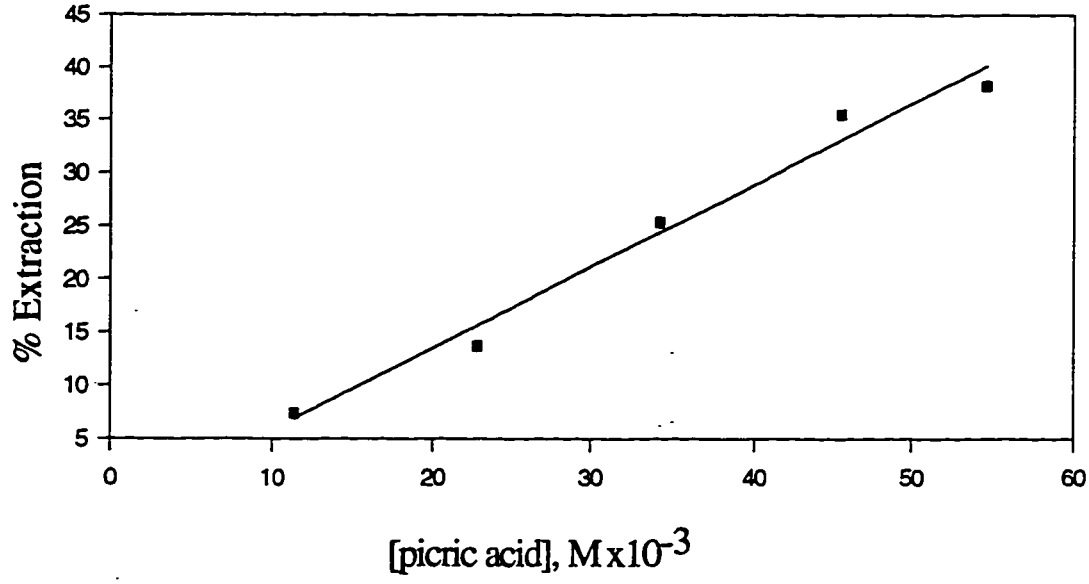


Fig. 3.18 Extraction of Eu^{3+} into 1,2-dichloroethane by PEG-600 at various picrate concentrations.

Table 3.19 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1165M PBDO-700.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
98.00	95.98	11.38	2.06
98.00	92.79	22.76	5.32
98.00	89.09	34.14	9.09
98.00	84.59	45.52	13.68
98.00	78.32	54.62	20.08

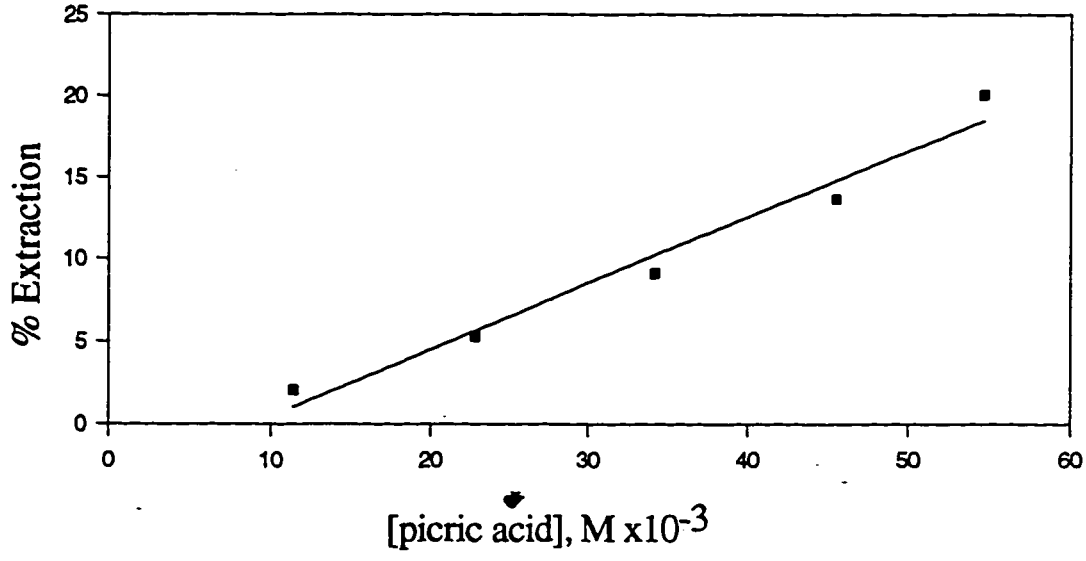


Fig. 3.19 Extraction of Eu^{3+} into nitrobenzene by PBDO-700 at various picrate concentrations.

Table 3.20 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1165M PBDO-700.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[picric acid], M x 10^{-3}	% Extraction
98.00	97.36	11.38	0.65
98.00	96.04	22.76	2.00
98.00	94.86	34.14	3.20
98.00	93.69	45.52	4.40
98.00	92.66	54.62	5.45

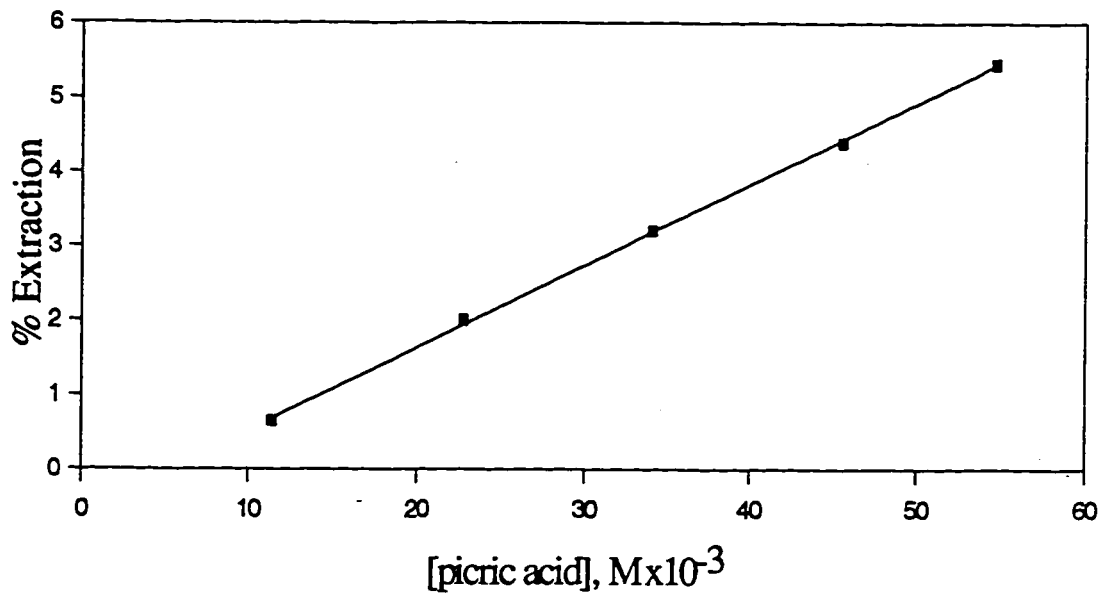


Fig. 3.20 Extraction of Eu^{3+} into 1,2-dichloroethane by PBDO-700 at various picrate concentrations.

The possibility of extracting picric acid as HPic from its aqueous solution into nitrobenzene phase was studied. It has been reported by Rais and Selucky[41], that at low concentrations of picric acid, only picrate anion extraction will take place and the picrate extraction constant K^{H^+,Pic^-} is 1.2 x 10^{-5}, but at concentrations greater than 10^{-3} M picric acid, molecular picric acid starts to extract.

The distribution equilibrium of picric acid, HPic between aqueous and nitrobenzene phases may be written as follows:

$$H^+ + Pic^- \overset{K^{H^+,Pic^-}}{\Longleftrightarrow} H^{+*} + Pic^{-*}$$

where K^{H^+,Pic^-} is the extraction constant of picrate which may be expressed as follows:

$$K^{H^+,Pic^-} = \frac{[H^{+*}][Pic^{-*}]}{[H^+][Pic^-]}$$

Thus, the distribution ratio of picric acid, HPic is,

$$D = \frac{[Pic^{-*}]+[HPic^*]}{[Pic^-]} = \frac{[Pic^{-*}]}{[Pic^-]} + \frac{[HPic^*]}{[Pic^-]}$$

Consequently,

$$D = \sqrt{K^{H^+,Pic^-}} + \frac{K^{H^+,Pic^-}[HPic^*][H^+]}{[Pic^{-*}][H^{+*}]}$$

That is

$$D = \sqrt{K^{H^+,Pic^-}} + \frac{K^{H^+,Pic^-}}{K^*_{HPic}}[H^{+*}]$$

where K^{*}_{HPic} is the dissociation constant of picric acid in nitrobenzene which was reported[42] as 1.26 x 10^8. Plotting D against [H^+] gives a straight line with a slope of

$$\frac{K^{H^+, Pic^-}}{K^{*}_{HPic}}$$

In this study, picric acid extraction was carried out by shaking aqueous solutions of picric acid (10 ml) of different concentrations with nitrobenzene (10 ml). The aqueous phase was then separated and the pH was measured at room temperature. Aqueous picric acid was considered to be completely ionized since its $K_a = 0.51$[43] at 25°C. Both the measured and calculated pH of the initial aqueous picric acid solutions were in good agreement confirming the assumption of almost complete dissociation of picric acid. The pH of the aqueous picric acid solution was measured by the glass electrode before and after shaking with nitrobenzene. The amount of H^+ extracted into the organic phase was computed by difference from the aqueous phase. Table (3.21) shows the calculated distribution ratios (D) for picric acid between water and nitrobenzene phase. Plotting D values against [H^+] left in the aqueous phase gave a straight line (Figure 3.21), with a slope of 1.0x10^3. K^{H^+, Pic^-} was computed from the slope (Figure 3.21) and found to be 1.3 x 10^{-5} , which is comparable to the reported value[43] (1.2 x 10^{-5}). The low value of K^{H^+, Pic^-} for picrate extraction indicates that picrate does not extract to the organic phase in the absence of metal ion in the aqueous phase and the ligand in the organic phase. This fact confirms that the picrate extracted

into nitrobenzene phase is only the portion associated with the complex (polyalkoxylate M^{+3} 3 picrate). It has been also reported previously[44] that when the concentration of picric acid exceeds 7.7 x 10^{-4} M the relationship between D and $[H^+]_{aq}$ deviates from linearity positively, indicating the possibility of having the molecular picric acid extracted to the organic phase along with the ion-pair.

Table 3.21 Distribution of picric acid between aqueous phase and the nitrobenzene phase.

$pH_{initial}$	$[H^+]_{initial}$ = [picric], M	pH_{final}	$[H^+]_{final}$ = [picric], M	$[H^{+*}]$, M	D = $[H^{+*}]/[H^+]$
4.15	7.08×10^{-5}	4.25	5.62×10^{-5}	1.46×10^{-5}	0.26
3.65	2.24×10^{-5}	3.80	1.58×10^{-4}	6.54×10^{-5}	0.41
3.50	3.16×10^{-4}	3.70	2.00×10^{-4}	1.17×10^{-4}	0.58
3.20	6.31×10^{-4}	3.45	3.55×10^{-4}	2.76×10^{-4}	0.78
3.10	7.94×10^{-4}	3.40	3.98×10^{-4}	3.96×10^{-4}	1.00

$[H^{+*}]$ = concentration of picric acid extracted into the nitrobenzene phase.

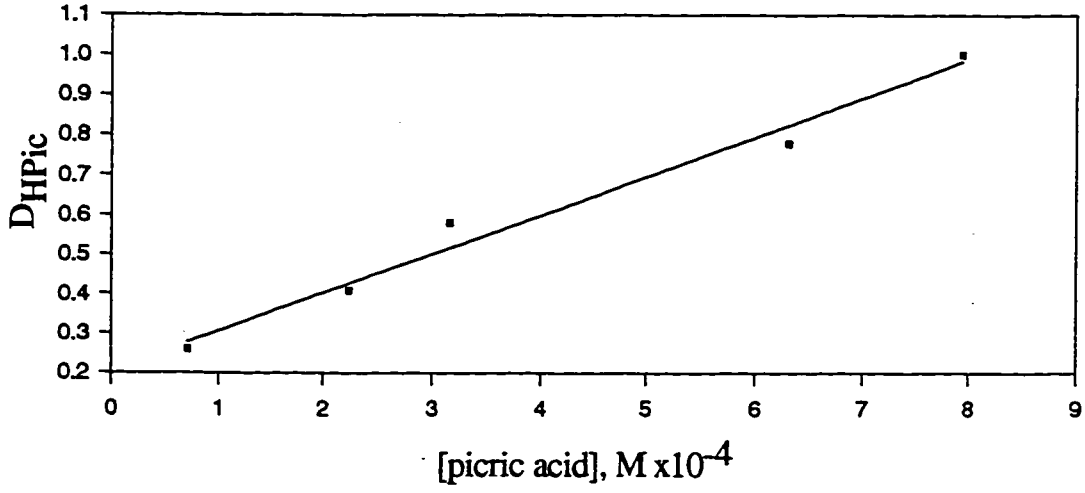


Fig 3.21 Distribution of picric acid between aqueous and nitrobenzene phases

3.2.3 Effect of pH on Extraction Efficiency

The optimum pH for the near quantitative extraction of lanthanides was ascertained by carrying out the extraction with 0.3 M polyoxyalkylenes in nitrobenzene or 1,2-dichloroethane, ~ 0.055M picric acid and 100ppm metal ion. pH was varied in the range of 1.5 to 5.5. The pH was adjusted by adding 0.1 M of NaOH. Attempts to raise the pH to higher values were not successful since the metal ions were hydrolyzed at such high pH values and a turbidy appeared in the aqueous solutions before extraction was carried out. The results showed that polyoxyalkylenes were suitable for near quantitative extraction of these cations in the pH range of 3.5 to 5.5. This is compatible with the results obtained previously for the extraction of Y^{3+} from Sr^{2+} using ionizable crown ether[45].

Tables 3.22 to 3.26 and Figures 3.22 to 3.26 show the extraction of the three metal ions, Eu^{3+}, Pr^{3+} and Er^{3+} from an aqueous phase of fixed picrate concentration (0.05384 M) and variable pH values into an organic phase containing 0.2954 M PPG-1,025. The extraction efficiency varies as a result of pH variation. The results shown indicate that the optimum pH for an efficient extraction lies within the range of 3 to 5. The results also, show the same trend of extraction mentioned previously without pH adjustment which is in the order of $Pr^{3+} > Eu^{3+} > Er^{3+}$ where it is about 92.6% in the case of Eu^{3+} (Table 3.22), 95.5% in the case of Pr^{3+} (Table 3.24), and 84.7% in the

case of Er^{3+}.(Table 3.26). It is obvious that the extraction at low pH values is much smaller than that at the optimum pH values. This behavior may be ascribed to extraction of protons at low pH values to the organic phase rather than the metal ion itself.

Tables 3.27 to 3.31 and Figures 3.27 to 3.31 show the percent extraction of europium from 0.05458 M picric acid at various pH values by 0.3010 M PEG-600 and 0.2821 M PBDO-700 in both nitrobenzene and 1,2-dichloroethane phases. The percent extraction of Eu^{3+} into nitrobenzene phase was near quantitative when PBDO-700 in nitrobenzene was used as the as the extractant (97%, Table 3.30) at the optimum pH. The trend of extraction efficiency into nitrobenzene organic phase was in the order of PBDO-700 > PPG-1025 > PEG-600. However, the extraction of the same metal ion, Eu^{3+}, under same conditions was in the order, PPG-1025 > PEG-600 > PBDO-700 when the organic diluent was 1,2-dichloroethane. Thus, the extraction selectivity may be reversed when a relatively low dielectric constant solvent is used as the organic phase.

Table 3.22 Extraction~100ppm Eu^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into nitrobenzene phase containing 0.2953M PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	pH	% Extraction
104.73	30.72	1.70	70.67
101.19	13.60	2.00	86.56
99.45	7.38	2.50	92.58
98.24	4.24	3.50	92.63
98.79	7.35	5.25	92.56

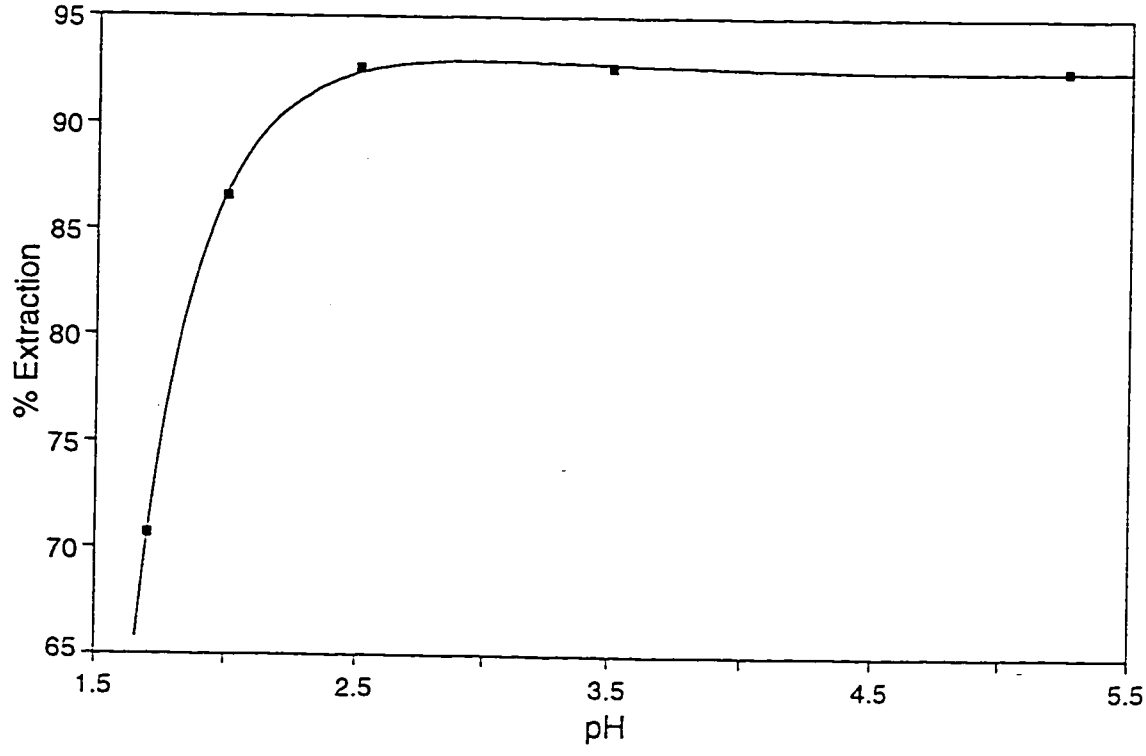


Fig. 3.22 Extraction of Eu^{3+} into nitrobenzene by PPG-1025 at various pH values.

Table 3.23 Extraction~100ppm Eu^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into 1,2-dichloroethane phase containing 0.30M PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	pH	% Extraction
104.73	45.40	1.70	56.65
101.19	22.66	2.00	77.60
99.45	14.03	2.50	85.89
98.24	13.32	3.50	86.44
98.79	12.50	5.25	87.35

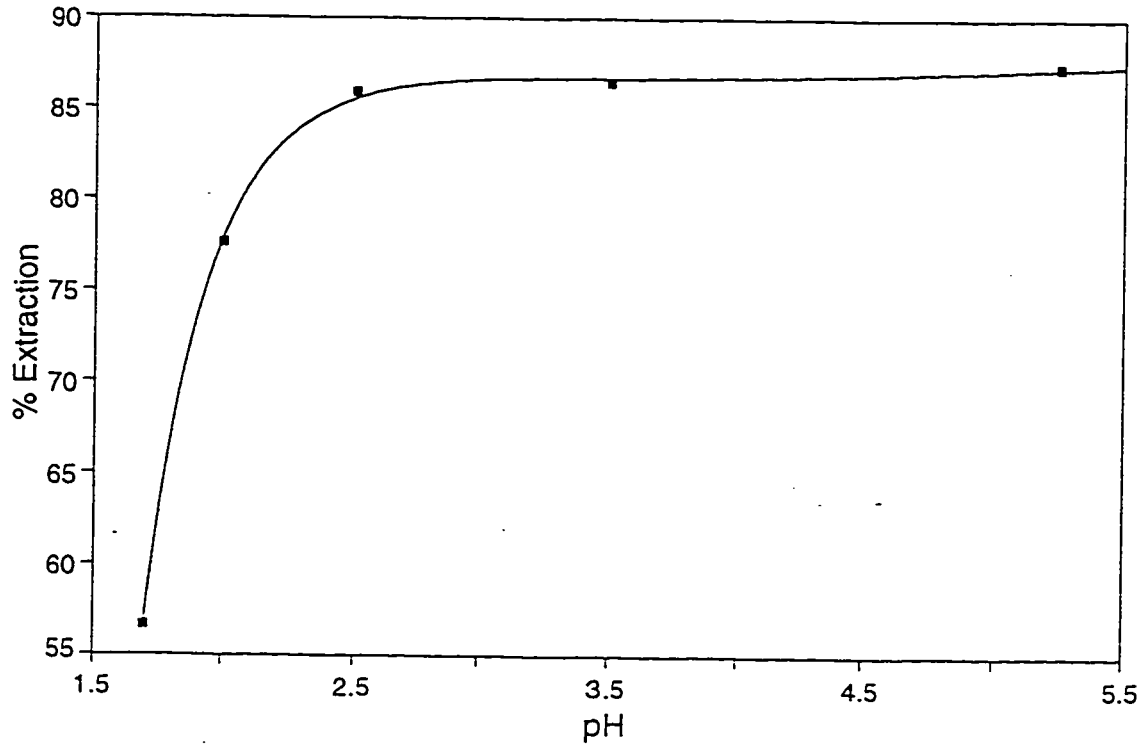


Fig. 3.23 Extraction of Eu^{3+} into 1,2-dichloroethane by PPG-1025 at various pH values.

Table 3.24 Extraction~100ppm Pr^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into nitrobenzene phase containing 0.2993M PPG-1025.

$[Pr^{3+}]$ before extraction, ppm	$[Pr^{3+}]$ after extraction, ppm	pH	% Extraction
97.00	20.17	2.30	79.21
98.90	6.98	3.20	92.94
100.00	4.97	3.90	95.03
99.00	4.47	4.70	95.48
98.90	4.45	5.55	95.50

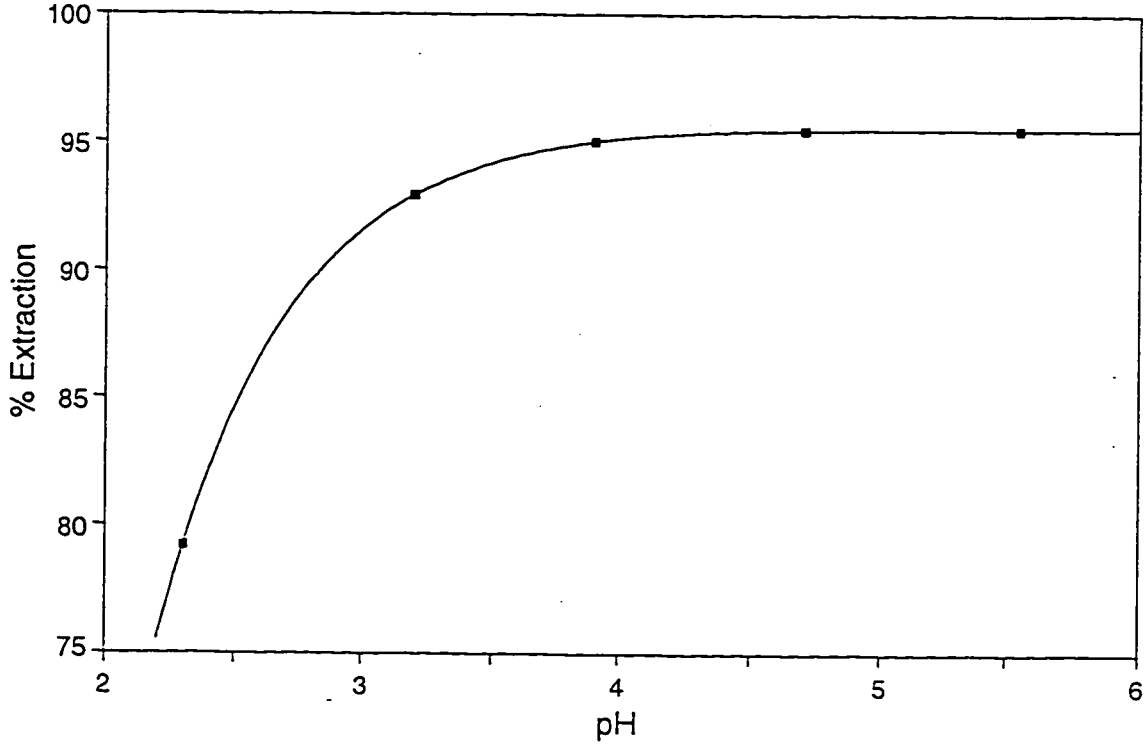


Fig. 3.24 Extraction of Pr^{3+} into nitrobenzene by PPG-1025 at various pH values.

Table 3.25 Extraction~100ppm Pr^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into 1,2-dichloroethane phase containing 0.30M PPG-1025.

$[Pr^{3+}]$ before extraction, ppm	$[Pr^{3+}]$ after extraction, ppm	pH	% Extraction
97.00	38.18	2.30	60.64
98.90	11.51	3.20	88.36
100.00	9.28	3.90	90.72
99.00	9.01	4.70	90.90
98.90	9.67	5.55	90.22

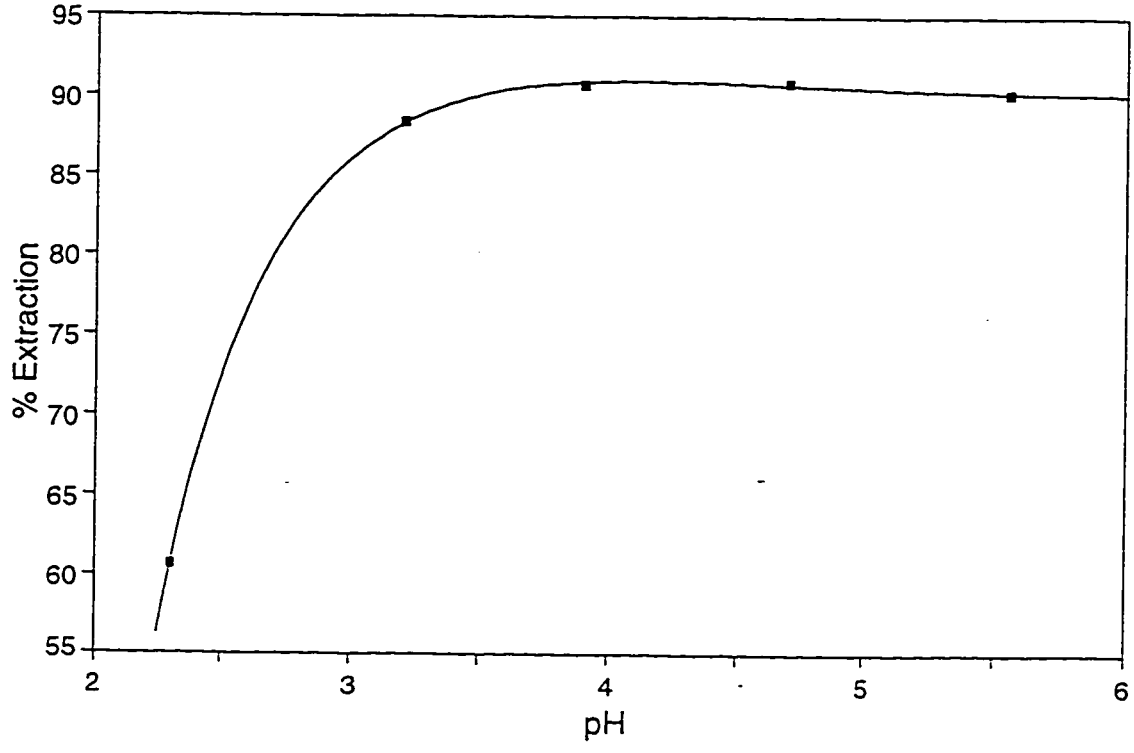


Fig. 3.25 Extraction of Pr^{3+} into 1,2-dichloroethane by PPG-1025 at various pH values.

Table 3.26 Extraction~100ppm Er^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into nitrobenzene phase containing 0.2992M PPG-1025.

$[Er^{3+}]$ before extraction, ppm	$[Er^{3+}]$ after extraction, ppm	pH	% Extraction
98.90	42.44	1.55	57.09
98.50	22.16	2.00	77.50
100.00	16.37	2.95	83.63
96.50	14.72	3.90	84.74
98.95	15.34	5.00	84.50

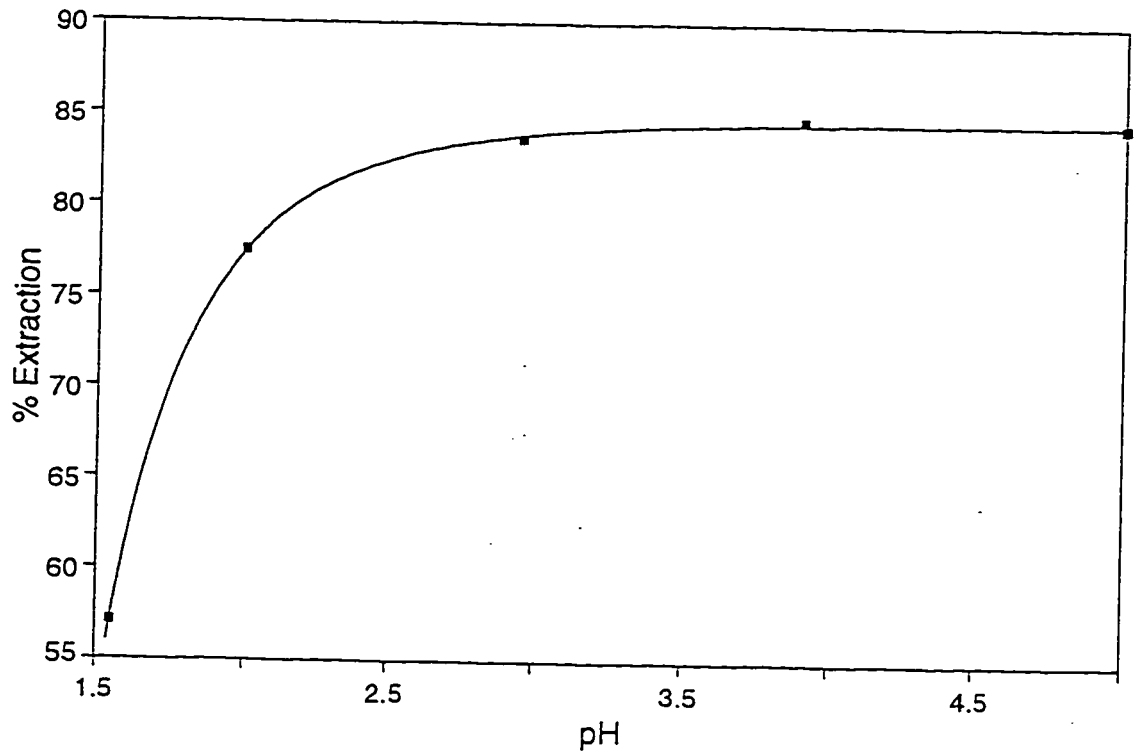


Fig. 3.26 Extraction of Er^{3+} into nitrobenzene by PPG-1025 at various pH values.

Table 3.27 Extraction~100ppm Er^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into 1,2-dichloroethane phase containing 0.30M PPG-1025.

$[Er^{3+}]$ before extraction, ppm	$[Er^{3+}]$ after extraction, ppm	pH	% Extraction
98.90	58.52	1.55	40.83
98.50	37.29	2.00	62.14
100.00	35.60	2.95	64.40
96.50	32.57	3.90	66.25
98.95	34.63	5.00	65.00

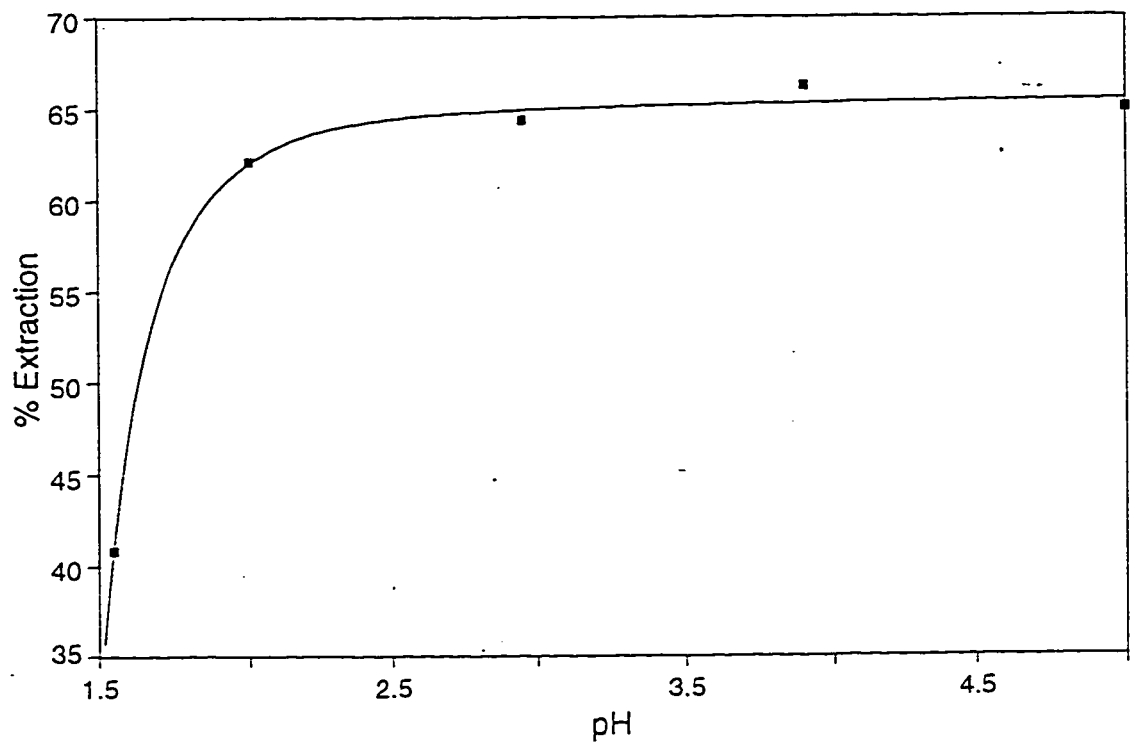


Fig. 3.27 Extraction of Er^{3+} into 1,2-dichloroethane by PPG-1025 at various pH values.

Table 3.28 Extraction~100ppm Eu^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into nitrobenzene phase containing 0.3010M PEG-600.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	pH	% Extraction
100.00	58.00	1.55	42.00
101.20	39.97	1.95	60.50
98.70	14.61	3.10	85.20
99.00	14.95	4.05	84.90
98.95	14.30	5.00	85.55

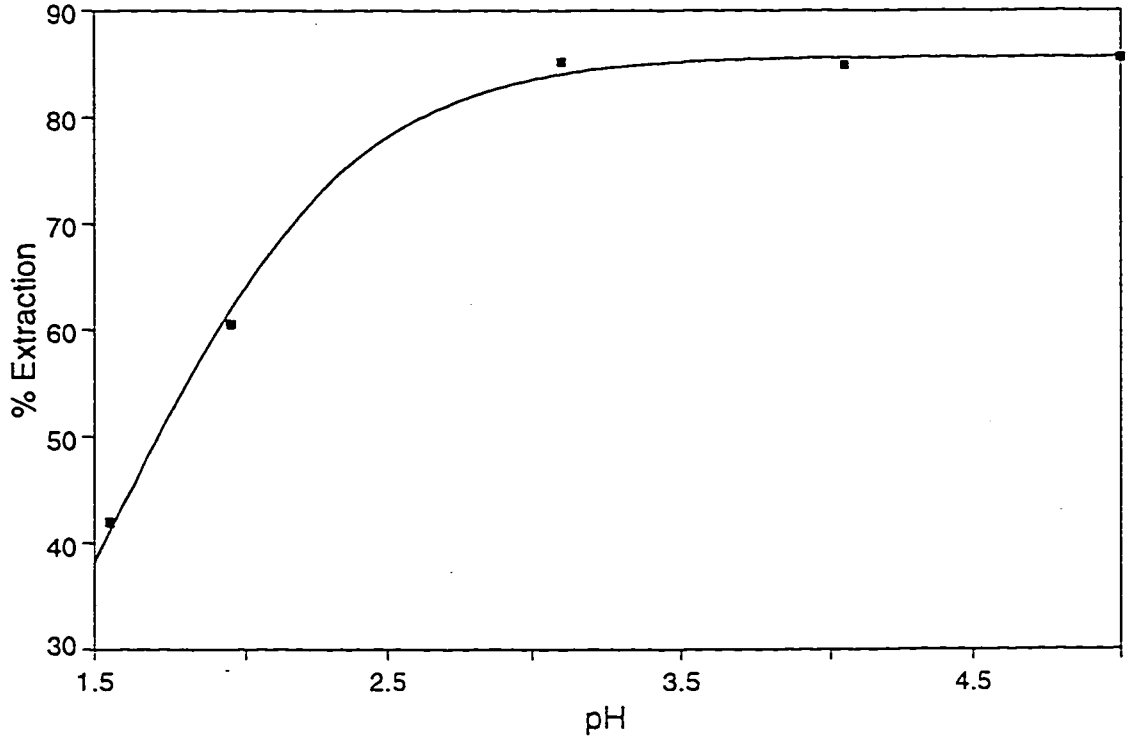


Fig. 3.28 Extraction of Eu^{3+} into nitrobenzene by PEG-600 at various pH values.

Table 3.29 Extraction~100ppm Eu^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into 1,2-dichloroethane phase containing 0.30M PEG-600.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	pH	% Extraction
100.00	86.00	1.55	14.00
101.20	40.34	1.95	60.14
98.70	34.54	3.10	65.00
99.00	34.45	4.05	65.20
98.95	34.73	5.00	64.90

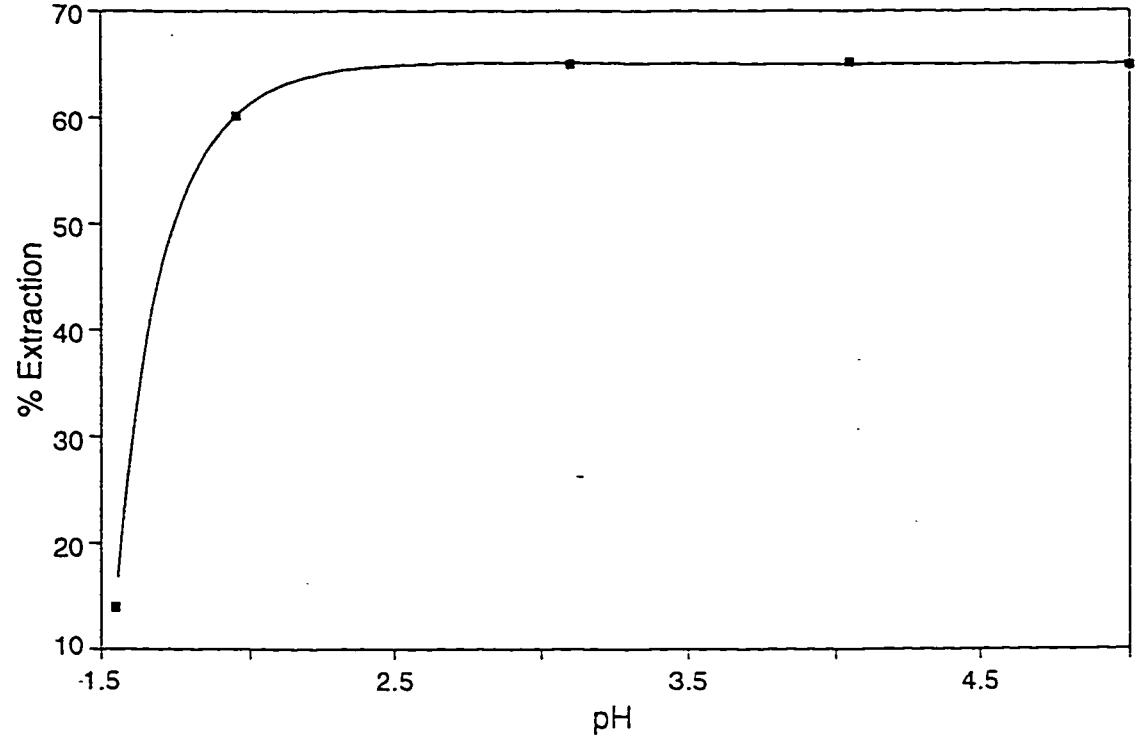


Fig. 3.29 Extraction of Eu^{3+} into 1,2-dichloroethane by PEG-600 at various pH values.

Table 3.30 Extraction~100ppm Eu^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into nitrobenzene phase containing 0.2821M PBDO-700.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	pH	% Extraction
96.70	89.06	1.55	7.90
100.10	4.87	1.95	95.13
102.50	3.22	3.10	96.86
97.80	2.95	4.05	96.98
98.72	2.87	5.00	97.09

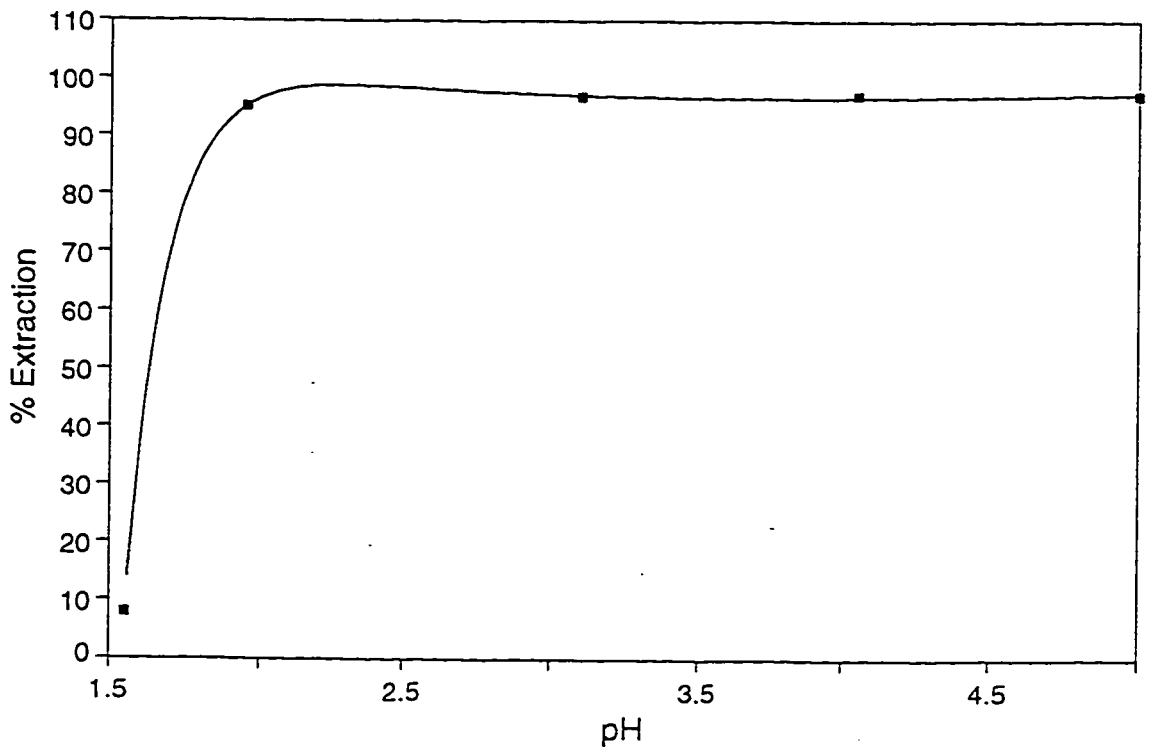


Fig. 3.30 Extraction of Eu^{3+} into nitrobenzene by PBDO-700 at various pH values.

Table 3.31 Extraction~100ppm Eu^{3+} from aqueous medium containing 0.0546M picric acid at variuos pH values into 1,2-dichloroethane phase containing 0.29M PBDO-700.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	pH	% Extraction
96.70	92.83	1.55	4.00
100.10	47.05	1.95	53.00
102.50	41.12	3.10	59.88
97.80	36.69	4.05	62.48
98.72	38.44	5.00	61.06

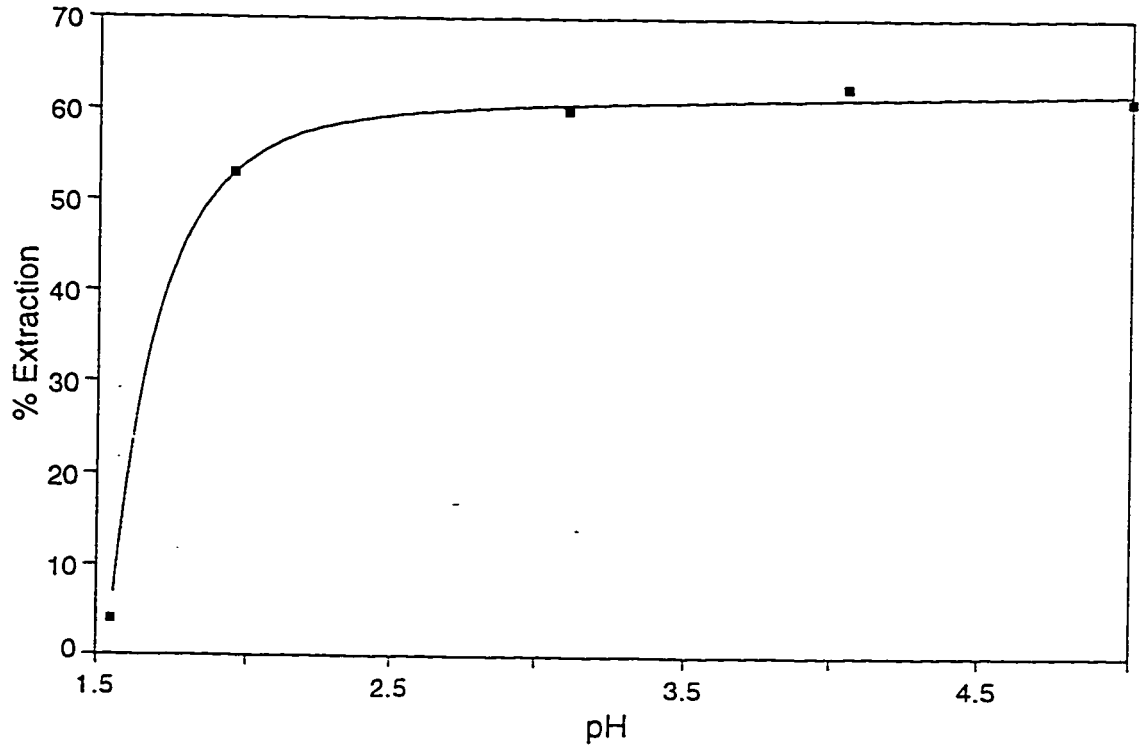


Fig. 3.31 Extraction of Eu^{3+} into 1,2-dichloroethane by PBDO-700 at various pH values.

3.2.4 Effect of the Type of Ligand and Its Concentration on Extraction Efficiency at the Optimum pH

Lanthanide metal ions (Eu^{3+}, Pr^{3+}, Er^{3+}) were extracted with 0.05 M picric acid at pH 4 - 4.5, that is within the optimum pH range, by varying the concentration of PPG-1025 in both nitrobenzene and 1,2-dichloroethane. The concentration of the polyoxyalkylene species was varied in the ranges 0.02 M - 0.3 M for PPG-1025, 0.02 - 0.4 M for PEG-600 and 0.01 - 0.3 M for PBDO-700. The results indicate a remarkable effect of the polyalkoxylate concentrations on the extraction efficiency particularly when the extraction efficiency is quite low. The extraction efficiency was relatively low in all extraction cases with 1,2-dichloroethane diluent (Tables 3.33, 3.35, 3.37, 3.39 and 3.41 and Figures 3.33, 3.35, 3.37, 3.39, and 3.41), in the case of extraction of erbium with both nitrobenzene and 1,2-dichloroethane diluents (Tables 3.36 and 3.37 and Figures 3.36 and 3.37) and in the case of the weak extractant PEG-600 (Tables 3.38 and 3.39 and Figures 3.38 and 3.39).The percent extraction continues to increase with polyoxyalkylene concentration in all of these cases. The extraction efficiency curves have been leveled off in the cases when the percent extraction was relatively high e.g., extraction of Pr^{3+} with PPG-1025 (Table 3.35 and Figure 3.35). However, the saturation has not been reached even with 0.3M in the cases when extraction efficiency was low; for example, when PEG-600 was used in the extraction of Eu^{3+} into 1,2-dichloroethane (Table 3.39 and Figure 3.39). This trend may be ascribed to the effect of polyoxyalkylene concentration on the extraction

efficiency equilibria, specially when the tendency for complex formation is relatively low. Tables 3.34 and 3. 40, Figures 3.34 and 3.40 show clearly that the extraction efficiency of Pr^{3+} was ~ 96% with 0.3 M PPG-1025 in nitrobenzene and that for Eu^{3+} was ~97% with 0.3 M PBDO-700 in nitrobenzene. Thus, the extraction in these two cases is almost quantitative and both PPG-1025 and PBDO-700 may be appropriate extractants for these metal ions.

3.2.5 Effect of Molecular Weigth of the Polyoxyalkylene on Extraction Efficency

The extraction of Eu^{3+} from an aqueous solution of 0.05 M picric acid at pH 4.5 into nitrobenzene or 1,2-dichloroethane phase containing 0.15 M PPG of two different molar masses, namely PPG-1025 and PPG-2000 has been carried out. The results are summarized in Table 3.42 which indicates that the extraction efficiency increases with the molar mass of PPG, that is, increasing of the number of alkylene oxide units. This is consistent with the litrature reports for the extraction of transition metal ions by various polyethylene and polypropylene glycols of different molar masses[5,46]. Extraction of alkali and alkaline earth metal ions by poly(oxyethylene)[47] , and extraction of alkali and alkaline earth metal ions with noncyclic poly(oxyethylene) derivatives[48]. The increase in extraction efficiency with the number of polyalkylene oxide units of polyoxyalkylene has been ascribed to the high hydrophopic property of the high molecular weight polyoxyalkylene.

Table 3.32 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into nitrobenzene phase containing various concentrations of PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
99.00	7.36	0.0206	92.56
99.00	8.12	0.0401	91.80
99.00	7.29	0.0945	92.64
99.00	9.60	0.2053	90.30
99.00	7.23	0.2939	92.70

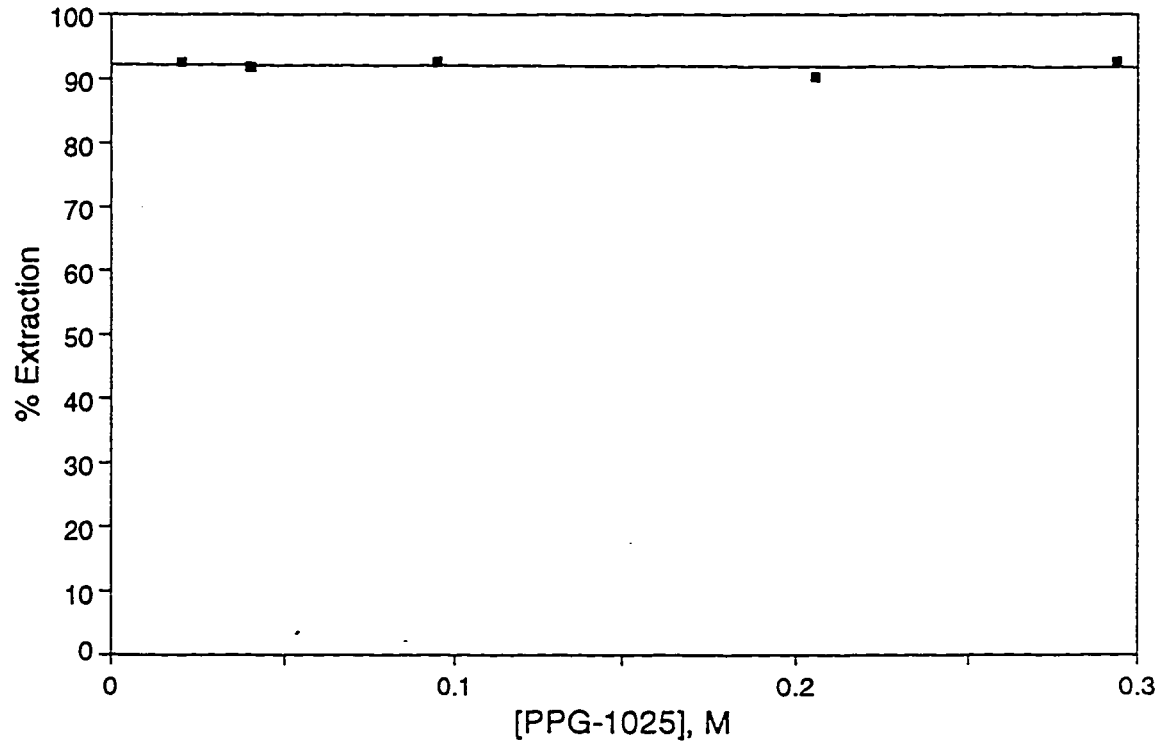


Fig. 3.32 Extraction of Eu^{3+} into nitrobenzene by PPG-1025 at pH 4.50

Table 3.33 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentrations of PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
99.00	61.99	0.0202	37.38
99.00	45.72	0.0406	53.82
99.00	31.52	0.0986	68.16
99.00	23.67	0.2058	76.09
99.00	12.52	0.2936	87.35

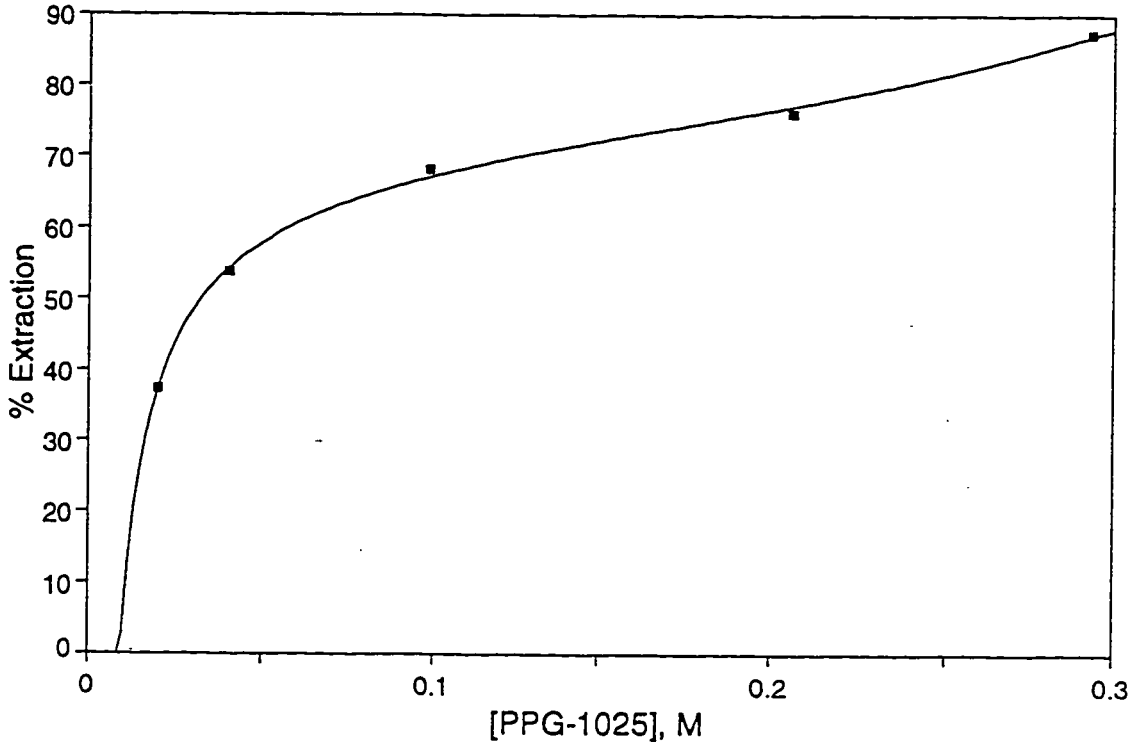


Fig. 3.33 Extraction of Eu^{3+} into 1,2-dichloroethane by PPG-1025 at pH 4.50

Table 3.34 Extraction of Pr^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into nitrobenzene phase containing various concentrations of PPG-1025.

$[Pr^{3+}]$ before extraction, ppm	$[Pr^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
99.57	7.51	0.0082	92.46
99.57	3.88	0.0302	96.10
99.57	3.75	0.0486	96.23
99.57	4.62	0.1030	95.36
99.57	4.23	0.2993	95.75

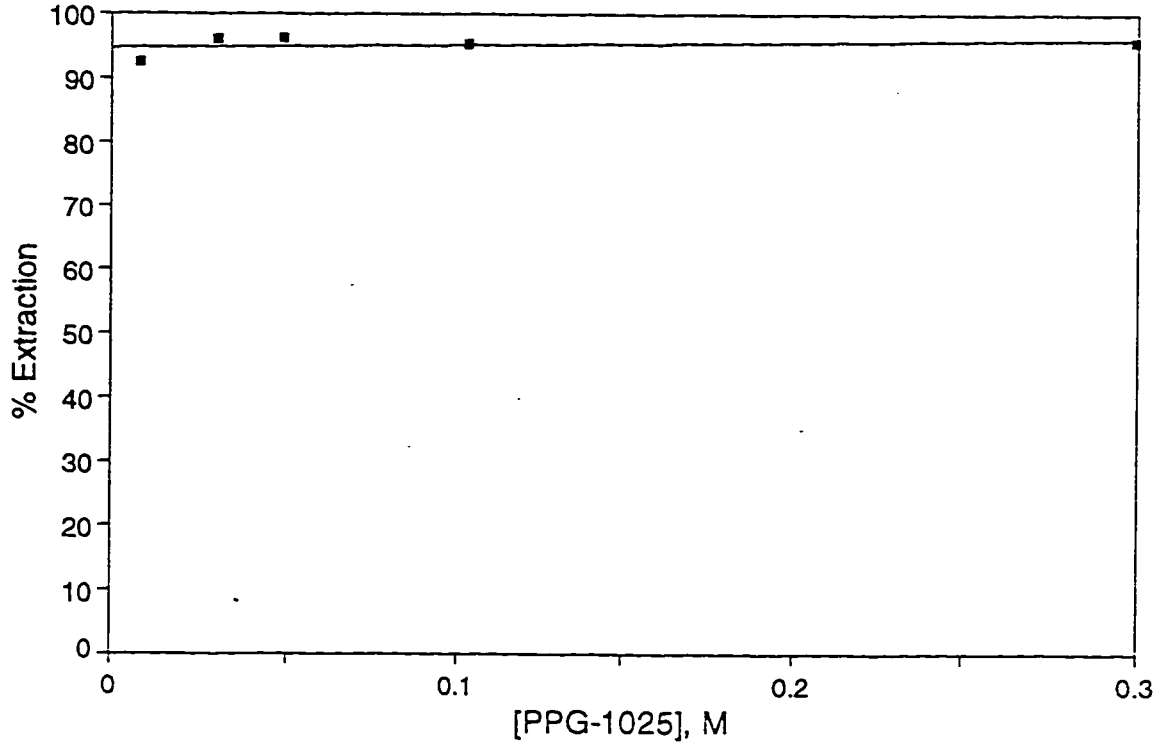


Fig. 3.34 Extraction of Pr^{3+} into nitrobenzene by PPG-1025 at pH 4.50

Table 3.35 Extraction of Pr^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentrations of PPG-1025.

$[Pr^{3+}]$ before extraction, ppm	$[Pr^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
99.57	57.09	0.0084	42.66
99.57	32.05	0.0276	67.81
99.57	23.38	0.0466	76.52
99.57	15.01	0.1028	84.93
99.57	8.75	0.3015	91.21

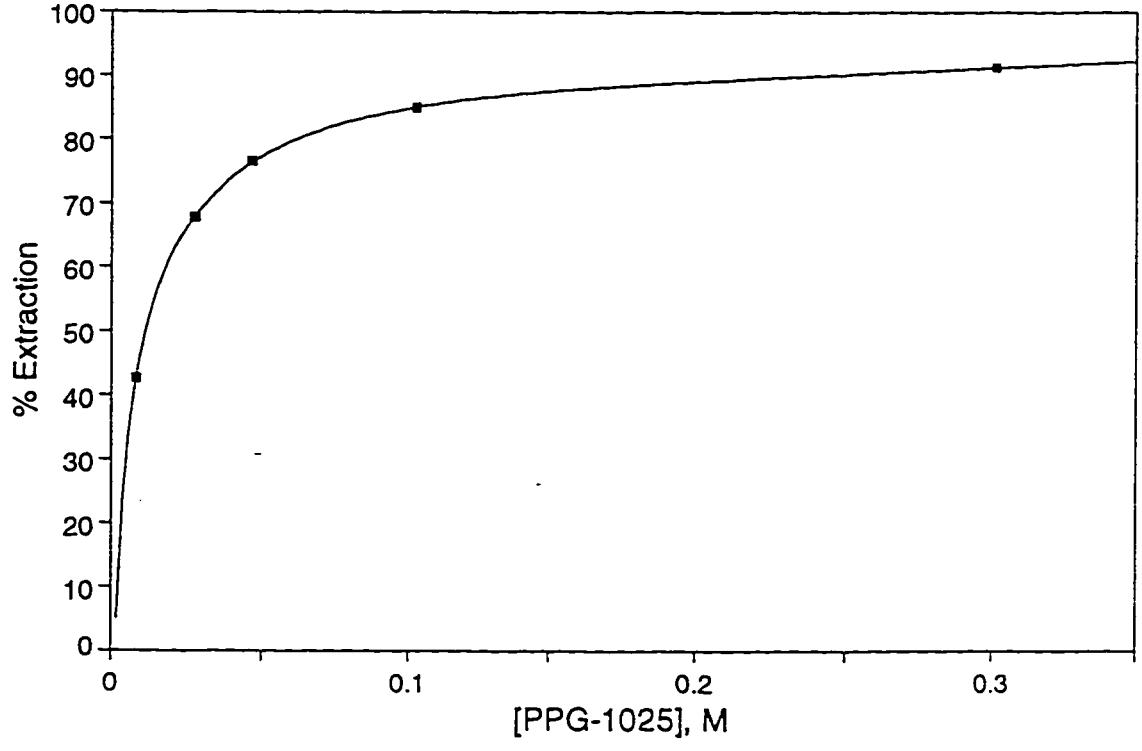


Fig. 3.35 Extraction of Pr^{3+} into 1,2-dichloroethane by PPG-1025 at pH 4.50

Table 3.36 Extraction of Er^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into nitrobenzene phase containing various concentrations of PPG-1025.

$[Er^{3+}]$ before extraction, ppm	$[Er^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
101.00	57.83	0.0087	42.74
101.00	31.59	0.0303	68.72
101.00	27.90	0.0477	72.38
101.00	25.24	0.1198	75.01
101.00	19.86	0.2992	80.34

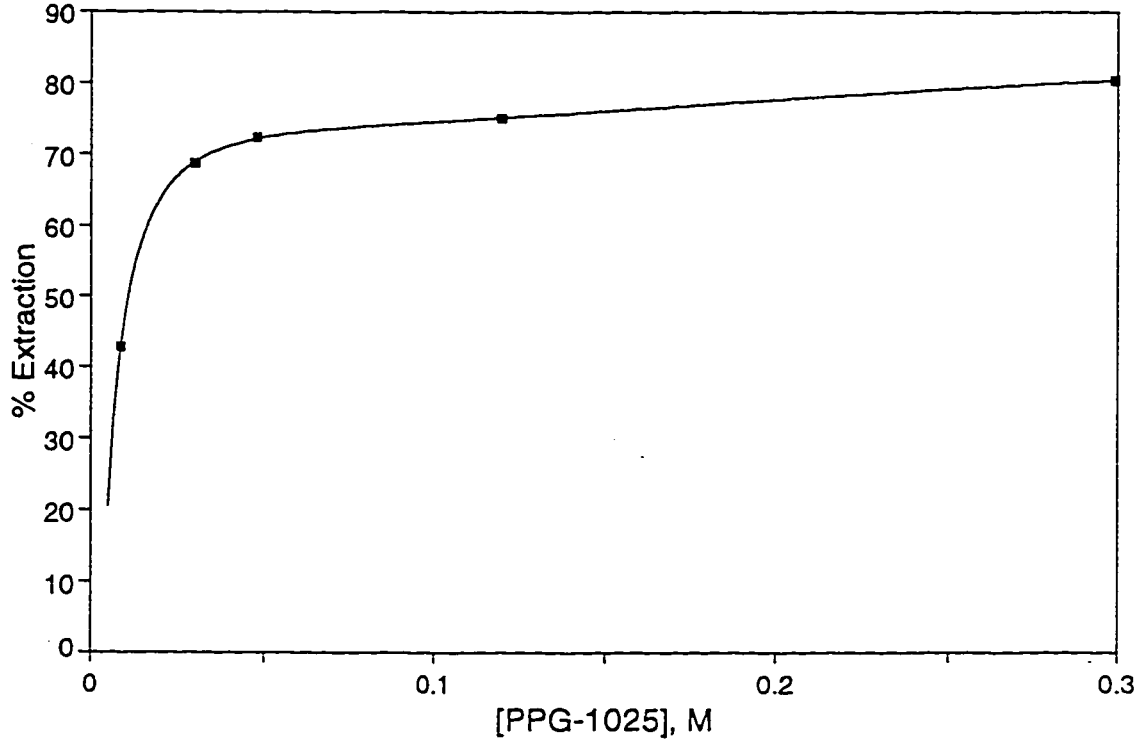


Fig. 3.36 Extraction of Er^{3+} into nitrobenzene by PPG-1025 at pH 4.50

Table 3.37 Extraction of Er^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentrations of PPG-1025.

$[Er^{3+}]$ before extraction, ppm	$[Er^{3+}]$ after extraction, ppm	[PPG-1025], M	% Extraction
101.00	92.74	0.0087	8.18
101.00	81.46	0.0298	19.35
101.00	75.87	0.0486	24.88
101.00	61.92	0.1215	38.69
101.00	38.96	0.3003	61.43

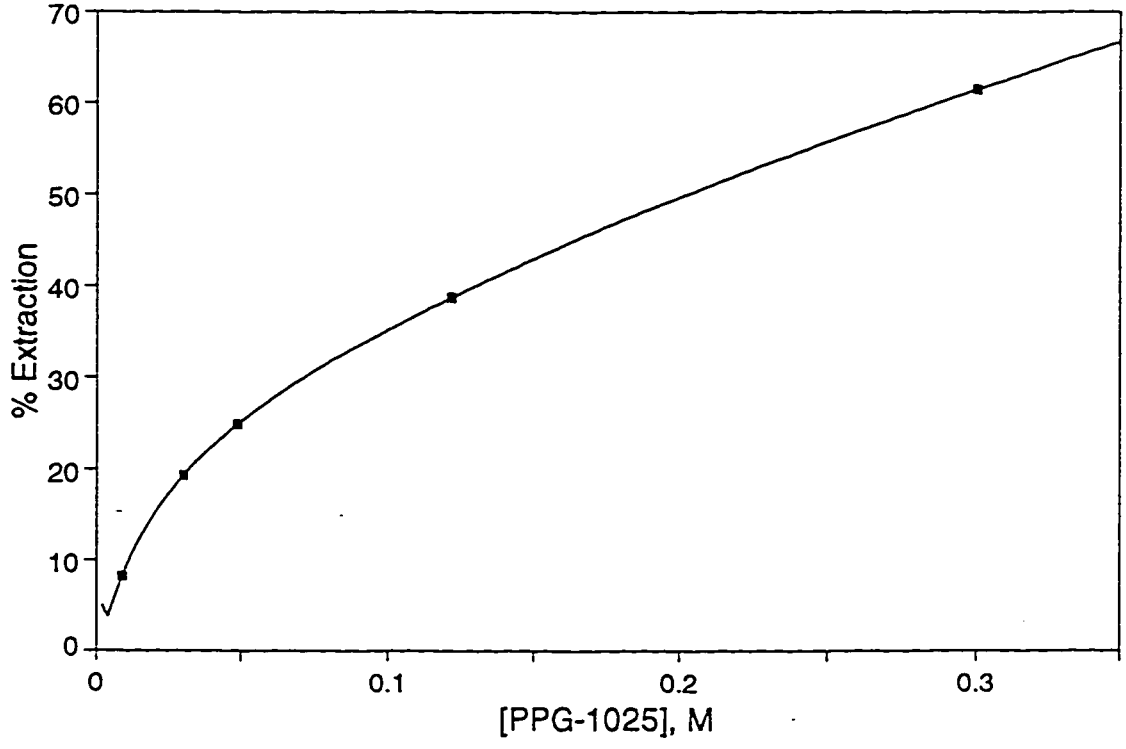


Fig. 3.37 Extraction of Er^{3+} into 1,2-dichloroethane by PPG-1025 at pH 4.50

Table 3.38 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into nitrobenzene phase containing various concentrations of PEG-600.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PEG-600], M	% Extraction
97.00	25.55	0.0215	73.66
97.00	17.91	0.0646	81.54
97.00	15.63	0.1076	83.89
97.00	14.83	0.2152	84.71
97.00	14.55	0.3000	85.00

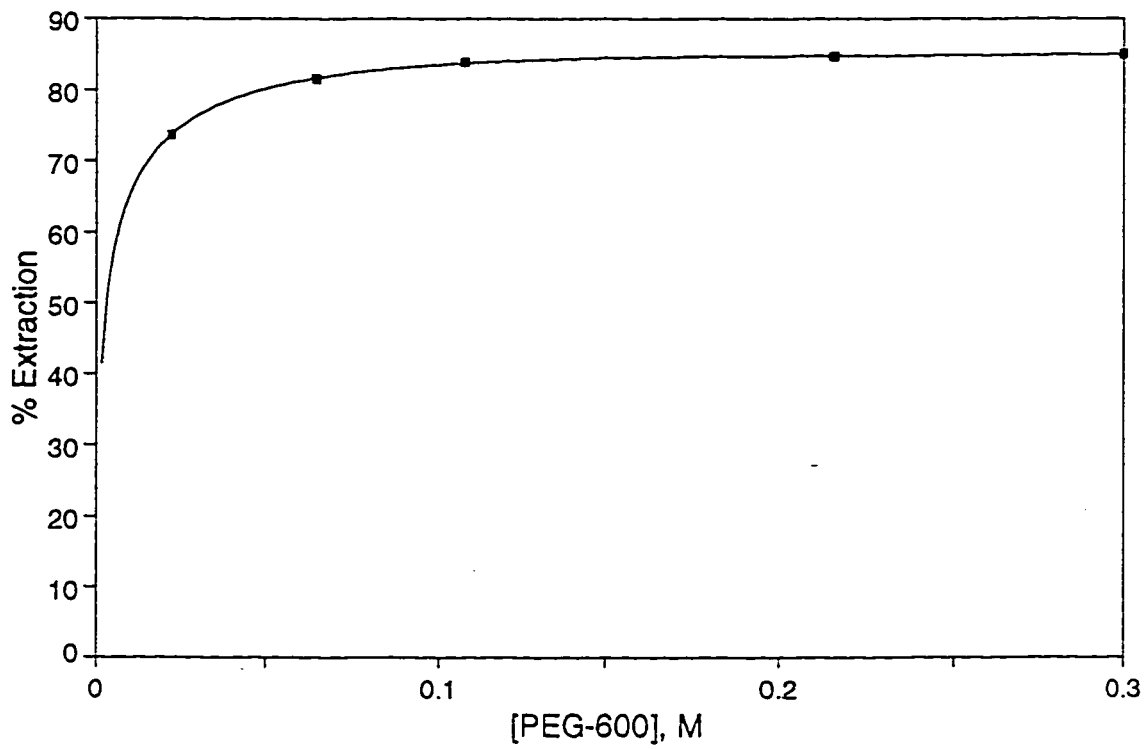


Fig. 3.38 Extraction of Eu^{3+} into nitrobenzene by PEG-600 at pH 4.50

Table 3.39 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentrations of PEG-600.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PEG-600], M	% Extraction
97.00	81.43	0.0218	16.05
97.00	64.78	0.0655	33.22
97.00	54.75	0.1092	43.56
97.00	45.05	0.2184	53.56
97.00	38.80	0.3003	60.00

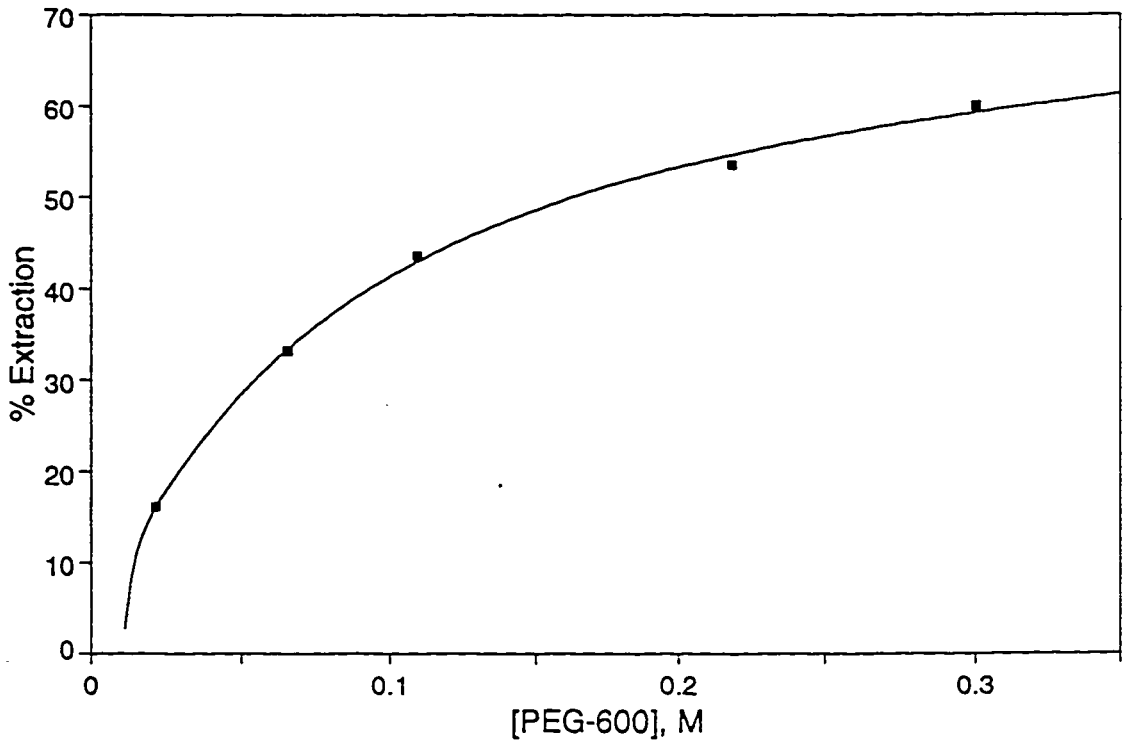


Fig. 3.39 Extraction of Eu^{3+} into 1,2-dichloroethane by PEG-600 at pH 4.50

Table 3.40 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into nitrobenzene phase containing various concentrations of PBDO-700.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PBDO-700], M	% Extraction
98.00	65.68	0.0113	32.98
98.00	60.84	0.0226	37.92
98.00	51.16	0.0338	47.80
98.00	24.08	0.1128	75.43
98.00	3.24	0.2921	96.69

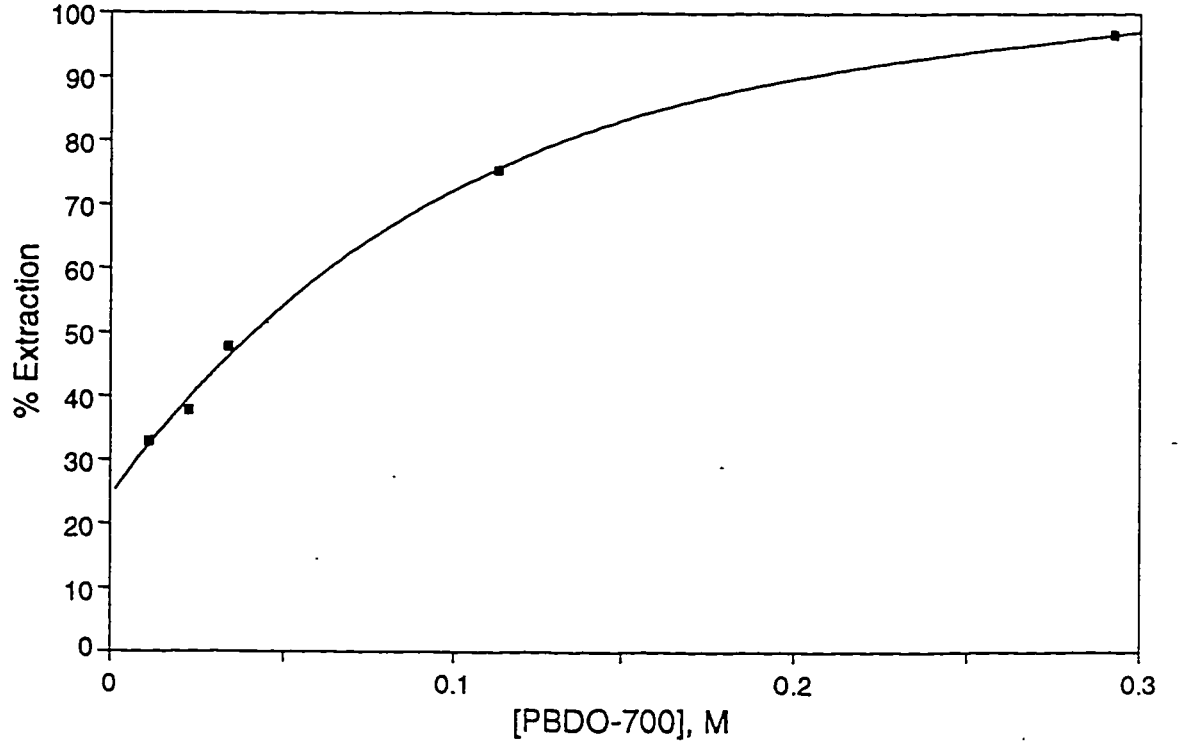


Fig. 3.40 Extraction of Eu^{3+} into nitrobenzene byPBDO-700 at pH 4.50

Table 3.41 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentration of PBDO-700.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	[PBDO-700], M	% Extraction
98.00	94.08	0.0115	4.00
98.00	93.91	0.0230	4.17
98.00	91.49	0.0345	6.64
98.00	79.97	0.1150	18.40
98.00	38.16	0.3003	61.06

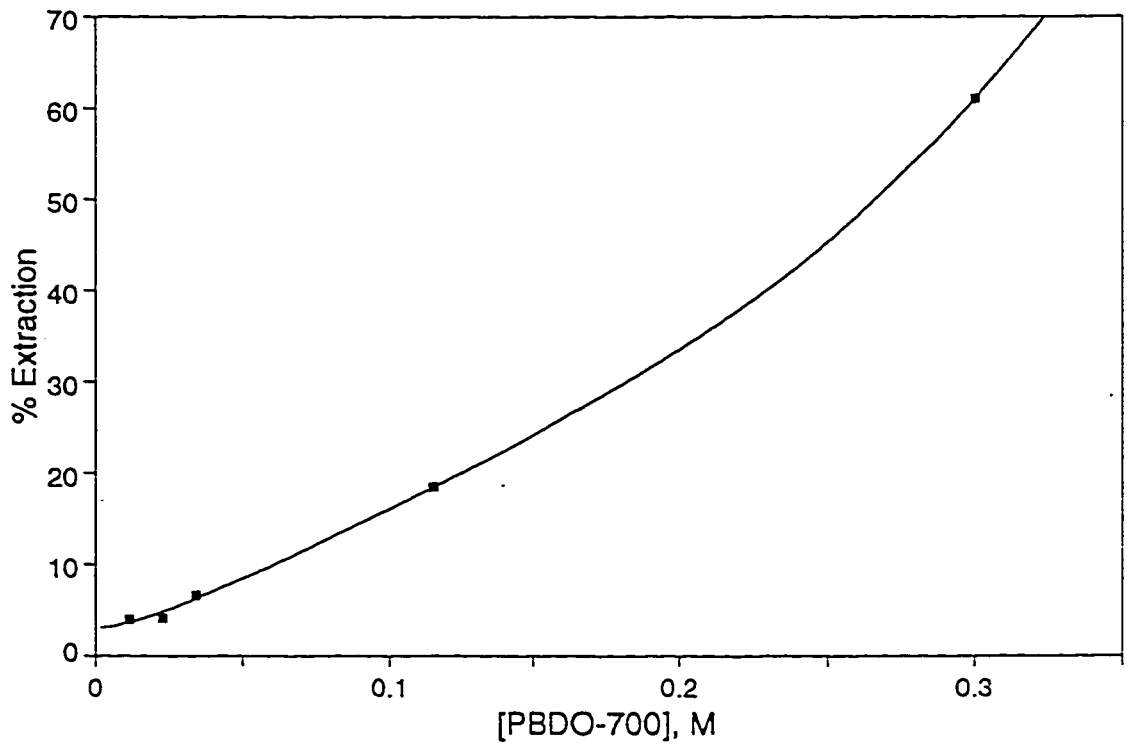


Fig. 3.41 Extraction of Eu^{3+} into 1,2-dichloroethane by PBDO-700 at pH 4.50

Table 3.42 Extraction of Pr^{3+}, Eu^{3+},and Er^{3+} ions from aqueous phase containing 0.0525 M picric acid at pH 4.50 into an organic phase of nirobenzene or 1,2-dichloroethane containing 0.15 M of PPG.

ligand	organic phase	% extraction		
		Pr^{3+}	Eu^{3+}	Er^{3+}
PPG-1,025	nitrobenzene	80.00	82.22	75.00
PPG-2,000	nitrobenzene	93.10	93.90	83.57
PPG-1,025	1,2-dichloroethane	67.00	65.64	40.00
PPG-2,000	1,2-dichloroethane	84.44	85.00	59.14

3.2.6 Effect of Metal Ion Concentration on Extraction Efficiency

Europium was extracted from aqueous solutions containing various concentrations of Eu^{3+}, about 0.033 M picric acid at a pH of 4.50 into the two organic diluents. The percent extraction of Eu^{3+} was almost constant in the case of nitrobenzene and 1,2-dichloroethane up to about 100 ppm Eu^{3+} (Tables 3.43 and 3.44 and Figures 3.42 and 3.43). The percent extraction of Eu^{3+} has decreased drastically

as its concentration exceeded 100 ppm in both nitrobenzene and 1,2-dichloroethane. This behavior may be attributed to the depletion of picrate anion from the aqueous phase which is necessary to enhance the extraction by forming ion-pair, metal ion-picrate, which is readily extracted by polyoxyalkylene system in the organic phase. Although the concentration of picrate is about ($3.3x10^{-2}$ M) 10 times as much as that of Eu^{3+} (about 100 ppm, that is ~ $2x10^{-3}$ M), it is sufficient to shift the extraction equilibrium to the ion-pair formation. Thus, increasing the picrate concentration by a certain mean may enhance the extraction of Eu^{3+} into the organic phase. If such a high concentration is to be extracted, a repetitive extraction procedure may be carried out and more picric acid is added and pH may be adjusted in each stage.

Table 3.43 Extraction of Eu^{3+} from aqueous medium containing various concentrations of Eu^{3+}, and 0.0331M picric acid at pH 4.50 into nitrobenzene phase containing 0.2936 M of PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	% Extraction
7.51	0.67	91.08
16.35	1.31	91.99
24.07	1.62	93.27
30.68	2.20	92.83
39.83	3.94	90.11
50.14	3.96	92.10
58.41	4.92	91.58
65.44	7.52	88.51
109.04	16.70	84.68
176.63	58.28	67.00
357.53	268.75	24.83

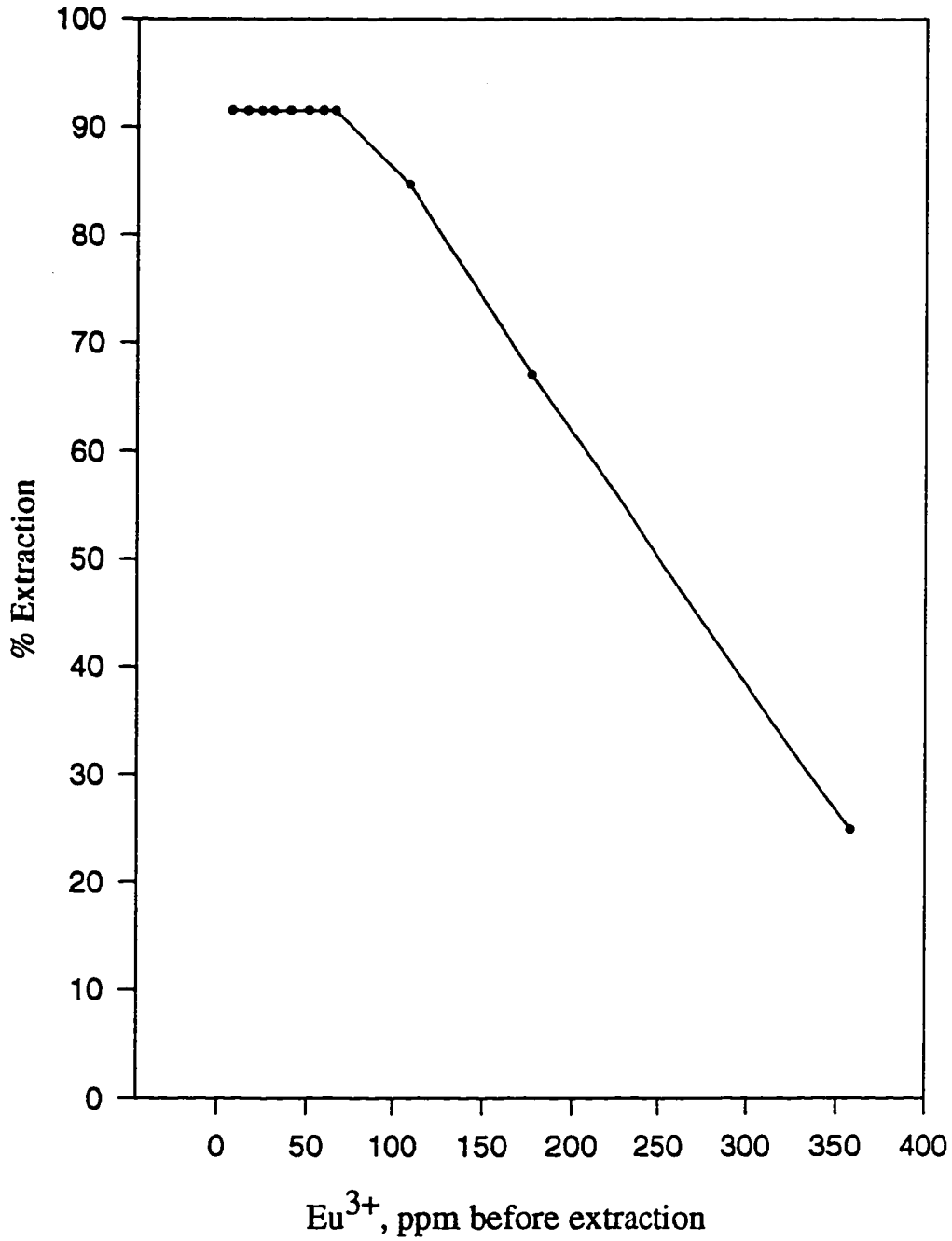


Fig. 3.42 Extraction of Eu^{3+} from aqueous phase at various concentrations of Eu^{3+} and 0.03M picric acid at pH 4.50 into nitrobenzene phase by 0.3M of PPG-1025.

Table 3.44 Extraction of Eu^{3+} from aqueous medium containing various concentrations of Eu^{3+}, and 0.0331M picric acid at pH 4.50 into 1,2-dichloroethane phase containing 0.2939 M of PPG-1025.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	% Extraction
7.51	1.63	78.30
16.35	2.90	82.26
24.07	3.82	84.13
30.68	5.78	81.16
39.83	7.73	80.59
50.14	9.11	81.83
58.41	11.29	80.67
65.44	14.00	78.61
109.04	24.78	77.27
176.63	60.05	66.00
357.53	229.72	35.78

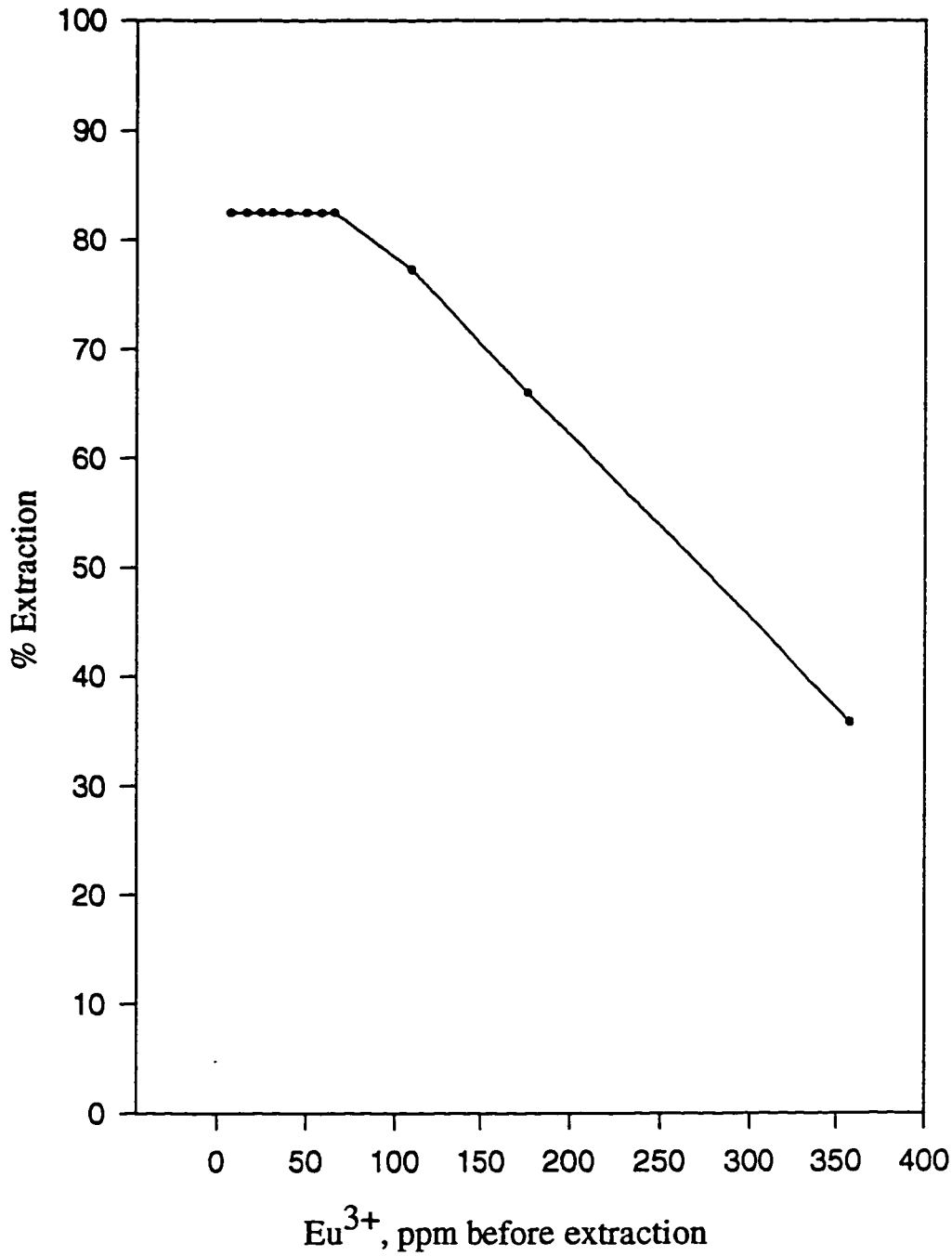


Fig. 3.43 Extraction of Eu^{3+} from aqueous phase at various concentrations of Eu^{3+} and 0.03M picric acid at pH 4.50 into 1,2-dichloroethane phase by 0.3M of PPG-1025.

3.3 Repetitive Extraction of Eu^{3+} by PPG-1025

Repetitive extraction experiments have been carried out to extract Eu^{3+} at various concentration levels (Table 3.45) from an aqueous phase of pH 4.5 into both nitrobenzene and 1,2-dichloroethane phase containing 0.030 M of PPG-1025. Fresh organic phase was used in the second extraction to check the possibility of extracting more of the metal ion left in the aqueous phase. Table 3.45 shows that most of the metal ion is extracted in the first extraction step. This confirms that the factor which determines the percent extraction is the picrate concentration in the aqueous phase. As a consequence of depletion of picrate anions in the aqueous phase more extraction will not be possible. The pH of the aqueous phase will also change and consequently the optimum extraction conditions are no longer available.

Table 3.45 repetitive extraction of Eu^{3+} from aqueous medium containing 0.0330M of picric acid at pH 4.50 into an nitrobenzene or 1,2-dichloroethane containing 0.2934M of PPG-1025.

organic phase	$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after 1^{st} extraction, ppm	$[Eu^{3+}]$ after 2^{nd} extraction, ppm
nitrobenzene	110.53	20.78	19.74
1,2-dichloroethane	110.53	29.24	28.47
nitrobenzene	368.58	230.12	226.50
1,2-dichloroethane	368.58	240.25	237.60

3.4 Optimum Conditions for Extraction

The optimum conditions for the extraction of lanthanide metal ions from an aqueous phase containing picric acid into organic phase containing a polyoxyalkylene system may be summarized as follows:

1. [Picric acid] $\geq$ 0.05 M

2. pH = 3 - 5

3. [polyoxyalkylene] > 0.05 M

with these conditions the lanthanide ions may be efficiently extracted into either of the organic phases studied. In addition, nitrobenzene with relatively high dielectric constant is a better medium for extraction compared to 1,2-dichloroethane.

3.5 Reproducibility of Extraction Measurements

The reproducibility of the extraction results was checked for the extraction of Eu^{3+} from an aqueous phase containing 0.052 M picric acid at a pH of 4.50 into an organic phase containing either nitrobenzene or 1,2-dichloroethane. The results are

summarized in tables 3.46 and 3.47. It is obvious that the measurements show excellent reproduciblity with relative standard deviation of 0.27% (Table 3.46) when the extraction conditions are at the optimum levels. However, the reproducibility has been checked for the extraction of Eu^{3+} from aqueous phases without pH adjustment (pH <2). Table 3.47 shows that the relative standard deviation is < ~2%.

Table 3.46 Reproducibility of extraction of Eu^{3+} from aqueous phase containing 0.0525 M picric acid at a pH of 4.50 into nitrobenzene phase containing 0.5258 M PBDO-700.

$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	% Extraction
83.50	7.30	91.26
83.50	6.80	91.86
83.50	7.10	91.50
83.50	7.20	91.38
83.50	6.90	91.74

Mean percent extraction is 91.53

Relative standard deviation is 0.27%

Table 3.47 Reproducibility of extraction of Eu^{+3} from aqueous phase containing 0.0483 M picric acid with a pH of <2 into nitrobenzene phase containing 0.1047M PPG-1025 and 1,2-dichloroethane phase containing 0.1017M PPG-1025.

Solvent	Number of replicates	$[Eu^{3+}]$ before extraction, ppm	$[Eu^{3+}]$ after extraction, ppm	% Extraction
Nitrobenzene	1	100.00	44.00	56.00
	2	100.00	45.20	54.80
	3	100.00	43.40	56.60
	4	100.00	44.00	56.00
	5	100.00	43.80	56.20
			Mean extraction=	***55.92%***
			Relative s.dev.=	1.20%
1,2-Dichloroethane	1	100.00	76.30	23.70
	2	100.00	77.50	22.50
	3	100.00	76.80	23.20
	4	100.00	75.00	25.00
	5	100.00	78.40	21.60
			Mean extraction=	***22.62%***
			Relative s.dev.=	***1.96%***

CHAPTER IV

COMPLEXING AFFINITY OF POLYOXYALKYLENES IN NITROBENZENE AND 1,2-DICHLOROETHANE WITH Eu^{3+}, Pr^{3+}, AND Er^{3+} METAL IONS

4.1 Extraction Equilibria

The complexing ability of neutral carriers with metal ions has been extensively studied by partitioning of their complexes between two immiscible solvents [8]. Also the equilibria governing the distribution processes have been treated in different ways.

Most of the reported methods to study the equilibria have been carried out by shaking aqueous solutions containing metal cation M^{Z+}, lipophilic anion ,for example, picrate anion ($\mathcal{X}^-$) and non-lipophilic anion $(Cl^-, NO_3^- or OH^-)$ with an organic solution containing a neutral carrier [8,45,49]. The most possible equilibrium may be written in the form:

$$M^{z+} + y\,L^{*} + z\,X^{-} \quad \Leftrightarrow \quad M\,L_y\,X_z^{*} \qquad (4.1)$$

Where M^{Z+} is the metal ion of charge z, L^* is the neutral carrier used (the asterisk refers to the organic phase), y is the number of moles of neutral carrier associated with one mole of the metal ion, X^- is the lipophilic anion (picrate ion) used to enhance the

extraction into the organic phase. $ML_yX_z^*$ is an associated ion-pair which may dissociate depending on the polarity of the organic phase. Since the partition of the non-lipophilic anion is very much small compared to that of the lipophilic anion, thus a negligible amount of it will be extracted to the organic phase[50]. The extraction equilibrium could be applied over a wide range of concentrations of metal ions and then extraction constant, K_{ex} could be estimated.

In the case of polyoxyalkylenes, the stiocheometry, y , is not a whole number ratio but it is a fraction since the molecule forms a helix configuration and wraps around the metal ion in a way that contain number of alkylene oxide units will be associated with one mole of metal ions. Thus, the extraction equilibrium for polyoxyalkylene system may be represented[6] by the following equation:

$$M^{z+} + \frac{b}{n}L + zX^- \Leftrightarrow ML_{b/n}X_z \qquad (4.2)$$

where b is the number of alkylene oxide units (AOU) associated with a mole of the metal cation, n is the average number of moles of AOU per a mole of the polyoxyalkylenes.

Assuming that the dissociation of the associated complexes or $ML_{\frac{b}{n}}X_z^*$ is negligible, then K_{ex} for the extraction equilibrium (eq 4.1) may be expressed by the following equation:

$$K_{ex} = \frac{[M L_{b/n} X_z^-]}{[M^{z+}][L]^{b/n}[X^-]^z} \tag{4.3}$$

Distribution ratio (D) is expressed by the ratio of the organic metal ion concentration $[M^{Z+}]$ to the aqueous metal concentration $[M^{Z+}]$ in all chemical forms, that is:

$$D = \frac{[M^{z+}]}{[M^{z+}]} \tag{4.4}$$

Thus, D is expressed as follows:

$$D = \frac{[M L_{b/n} X_z^-]}{[M^{z+}] + [M L_{b/n}^{z+}]} \tag{4.5}$$

assuming that the dissociation of the ion-pair, $ML_{b/n}X_z$ in the organic phase is negligible and the partitioning of the neutral carrier (polyoxyalkylene) into the aqueous phase is negligible, consequently $[M^{z+}] >> [ML_{b/n}^{z+}]$. Hence, the distribution ratio will be expressed by the following equation:

$$D = \frac{[M L_{b/n} X_z^-]}{[M^{z+}]}$$

Introducing D into K_{ex} expression in equation 4.3 gives:

$$K_{ex} = \frac{D}{[L]^{b/n}[X^-]^z} \tag{4.6}$$

Re-arranging equation 4.6 and taking the log of both sides gives:

$$\log K_{ex} + \frac{b}{n}\log[L] = \log \frac{D}{[X^-]^z} \tag{4.7}$$

The stoichiometry of metal-picrate ion-pair can be elaborated more by considering

the dissociation of picric acid ,HX, in the aqueous phase according to the following equation:-

$$HX \quad \Leftrightarrow \quad H^+ + \quad X^- \qquad ; K_a = \frac{[H^+][X^-]}{[HX]} \qquad (4.8)$$

Assuming that $[HX] > [M^{3+}]$ and $[H^+] = [X]$, then

$$K_a[HX] = [H^-][X^-] = [X^-]^2 \qquad (4.9)$$

$$[X^-] = \sqrt{K_a[HX]} \qquad (4.10)$$

subtitute the value of $[X^-]$ in equation 4.7 will give ,

$$\log K_{ex} + \frac{b}{n}\log[L^*] = \log \frac{D}{K_a^{z/2}[HX]^{z/2}} \qquad (4.11)$$

Another an arrangement gives,

$$\log D = \log K_a^{Z/2} + \log K_{ex} + \frac{b}{n}\log[L^*] + \log[HX]^{Z/2} \qquad (4.12)$$

The terms K_a , K_{ex} are expected to be constants. Hence, when log D is plotted (ordinate) against log[L^*] (abscissa) will give a straight line with a slope of b/n and intercept of $\log K_{ex} + \log K_a^{z/2} + \frac{z}{2}\log[HX]$; taking into consideration that the experiments have been carried out under the conditions that [HX] and pH are constants.

On the other hand, if the ligand concentration ,[L^*], in the organic phase is kept constant with the picric acid concentration ,[HX], is varied , and logD is plotted

against log[HX], a straight line with a slope of z/2 would be expected where z is the number of moles of picrates associated with one mole of metal ion in the metal-picrate ion-pair. From the two plots mentioned above the stoichemetry of the complex $ML_{b/n}X_z^*$ could be obtained.

4.2 Stoichiometry of $ML_{b/n}X_z$ Ion-Pair with Respect to the Ligand

Stiochemiometry of the extracted Eu^{3+}, Pr^{+} and Er^{3+} ion-pairs with PEG-600, PPG-1025 and PBDO-700 has been estimated by carrying out extraction experiments in which 100 ppm of the metal ion has been extracted individually into nitrobenzene or 1,2-dichloroethane phase containing varied concentrations of the Ligand. Since $[L^*]_{initial}$ was in the range of about 0.01 to 0.3M, and $[M^{3+}]_{initial}$ was about 6.70×10^{-4} (100ppm), thus $[L^*]_{initial} >> [M^{3+}]_{initial}$. That is, $[L^*]$ at equilibrium is almost same as the initial value. Also, the concentration of picric acid was kept constant at about 0.055M, and the pH of the aqueous medium was either kept without adjustment (That is <2) or at the optimum value used for extraction, namely, about 4.5. Thus, logD was calculated for various polyoxyalkylenes and plotted against $\log[L^*]$.

The number of alkyleneoxide units was calculated from the molar mass for each polyoxyalkylene. For example, the number of AOU was calculated for PPG1025,

$HO-(\underset{\underset{CH_3}{|}}{CH}-CH_2-O)_n-H$, as follows:

Molar mass of propyleneoxide units = 1025 - 18 = 1007

Molar mass of each propylene oxide unit = 58

Number of propyleneoxide units per a molecule of PPG-1025, $n=\frac{1007}{58}=17.40$.

Consequently, the stoichiometry b/n can be calculated from the slope. In a similar treatment the number of ethylene oxide units (EOU) for PEG-600 was found to be 13.2 and the number of butadiene oxide units (BDOU) was found to be 10.

Consequently, the distribution ratio,D, has been calculated from the data in the tables of chapter 3, and log D values were plotted against logarithm of polyoxyalkylene cocentrations. The results are shown in Tables 4.1 to 4.17 and Figures 4.1 to 4.17. Some cases have been disregarded because the percent extraction was reached to its limiting value ,that is, a point at which no more metal ion has been extracted (Figures 3.32, 3.34 & 3.38) although the concentration of polyoxyalkylene is significantly high. However, the curves in which the limiting percent extraction has been reached (Figures 4.16 & 4.17), at high polyoxyalkylene concentrations, were assesed on the bases of the straight line portion only, that is, the concentrations which did show an extraction limitation in the organic phase.

Table 4.1 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations of PPG-1025 (data are taken from Table 3.1).

% Extraction	D	Log[L*]	Log D
11.20	0.1261	-2.0862	-0.8992
25.79	0.3475	-1.5200	-0.4590
32.56	0.4828	-1.3134	-0.3162
54.31	1.1887	-0.9872	0.0750
72.46	2.6311	-0.5327	0.4201

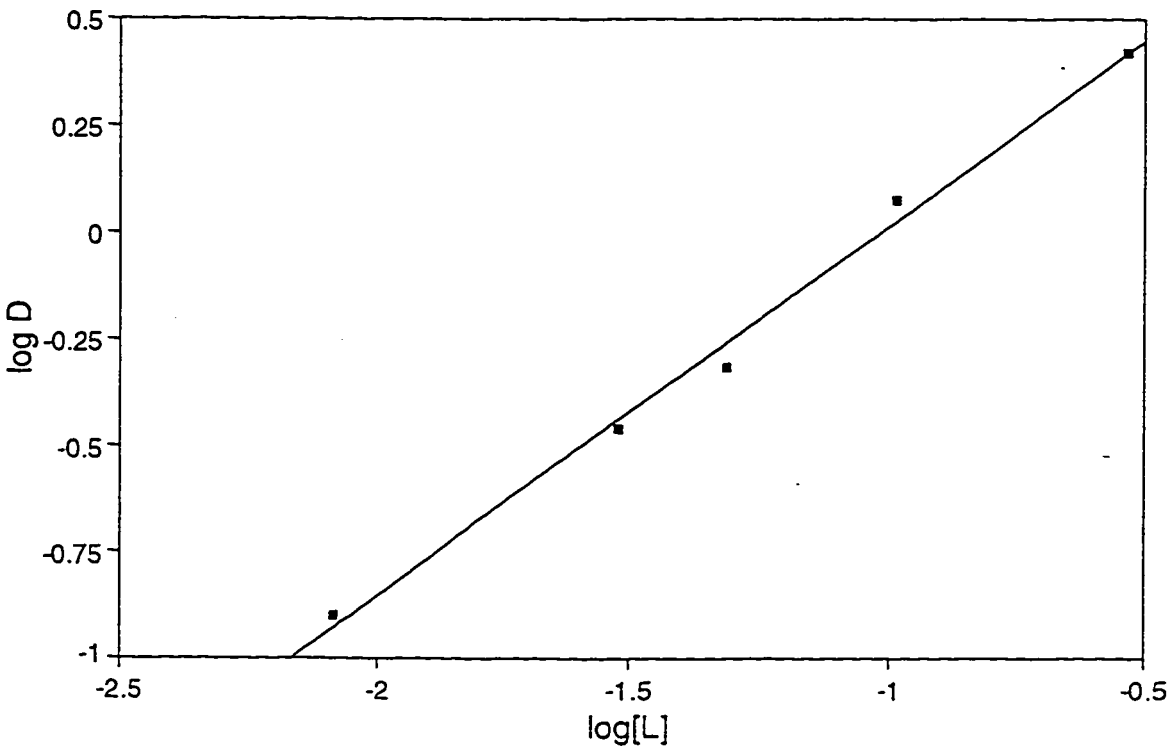


Fig 4.1 Log D versus log[L*] for Eu^{3+} extracted by PPG-1025 in nitrobenzene

Table 4.2 Extraction of Pr^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations of PPG-1025 (data are taken from Table 3.2).

% Extraction	D	Log[L*]	Log D
29.50	0.4184	-1.6861	-0.3784
4294	0.7525	-1.3969	-0.1235
58.27	1.3964	-1.0246	-0.1450
73.28	2.7425	-0.6876	0.4381
78.55	3.6620	-0.5322	0.5637

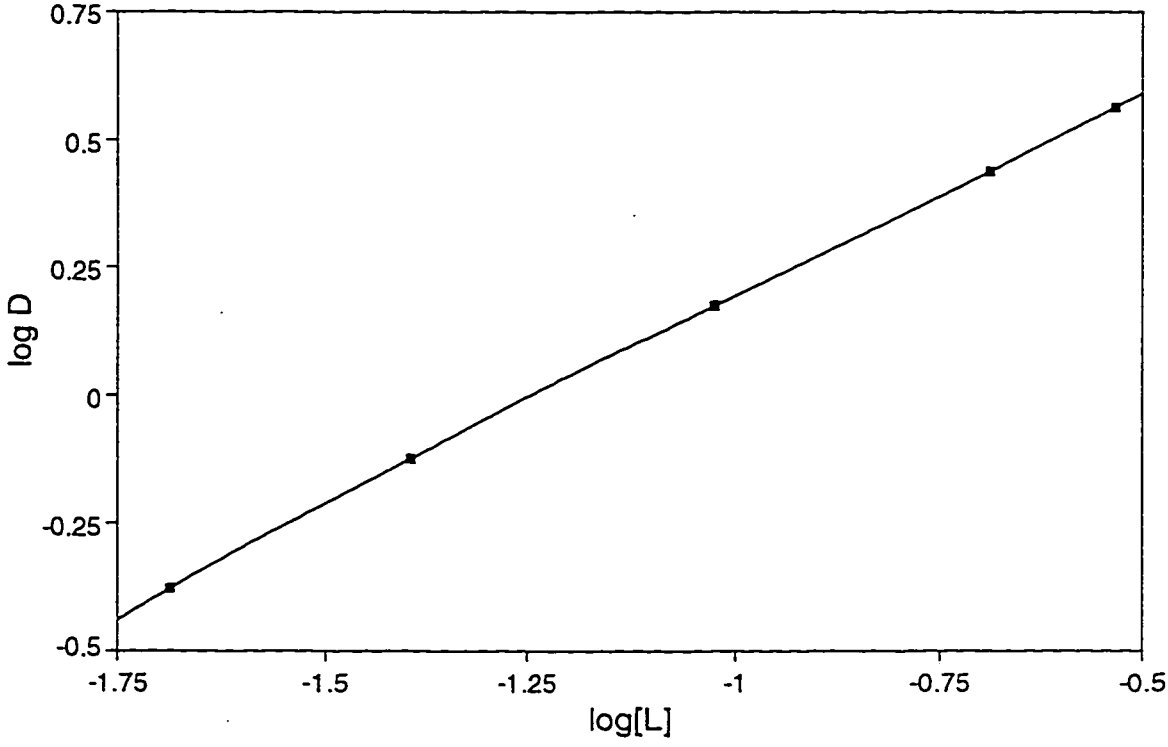


Fig 4.2 Log D versus log[L*] for Pr^{3+} extracted by PPG-1025 in nitrobenzene

Table 4.3 Extraction of Er^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations of PPG-1025 (data are taken from Table 3.3).

% Extraction	D	Log[L*]	Log D
6.76	0.0725	-2.0506	-1.1397
14.62	0.1712	-1.5171	-0.7665
20.77	0.2622	-1.3242	-0.5814
36.18	0.5670	-0.9215	-0.2464
51.90	1.0789	-0.5240	0.0330

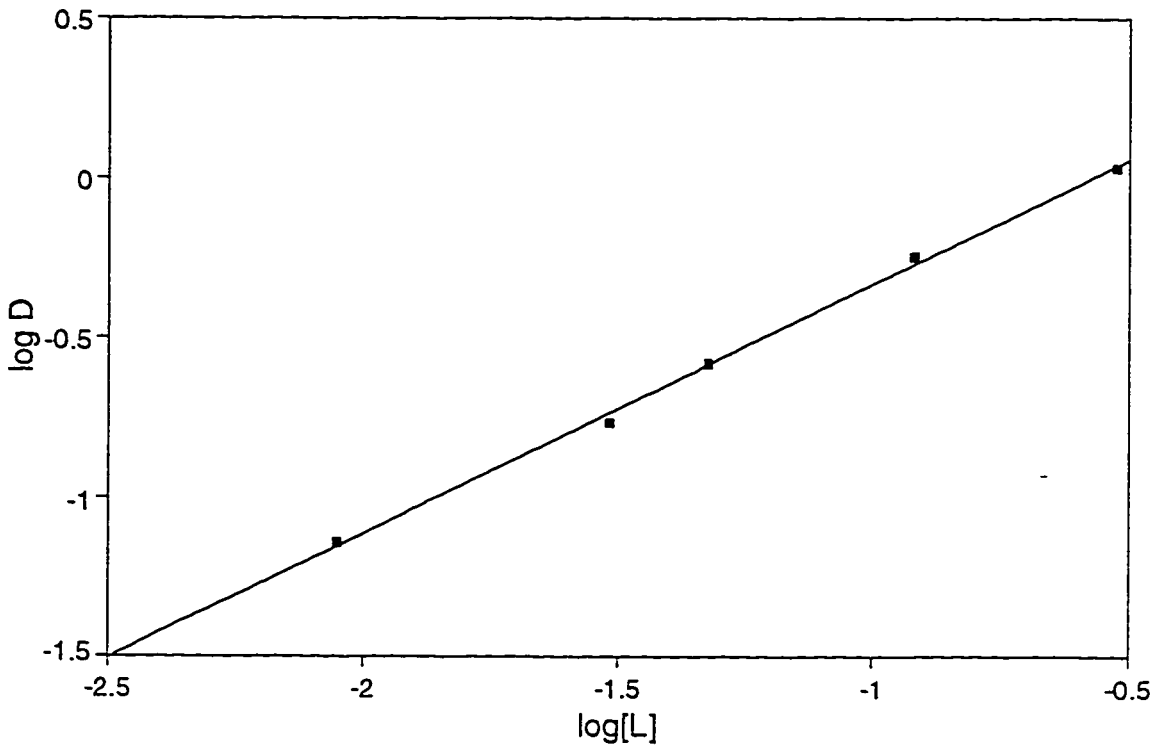


Fig 4.3 Log D versus log[L*] for Er^{3+} extracted by PPG-1025 in nitrobenzene

Table 4.4 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations of PEG-600 (data are taken from Table 3.4).

% Extraction	D	Log[L*]	Log D
11.55	0.1306	-1.6737	-0.8841
18.37	0.2250	-1.1898	-0.6478
27.38	0.3772	-0.9682	-0.4234
38.06	0.6145	-0.6672	-0.2115
41.00	0.6949	-0.5229	-0.1581

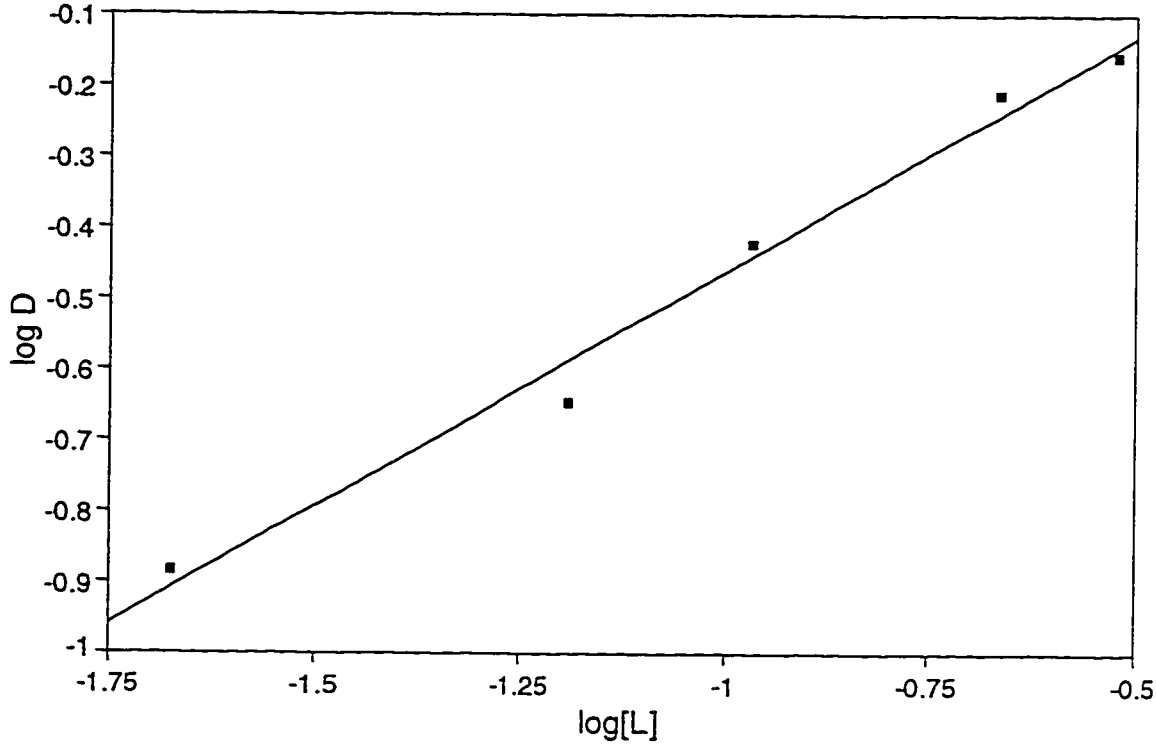


Fig 4.4 Log D versus log[L*] for Eu^{3+} extracted by PEG-600 in nitrobenzene

Table 4.5 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into nitrobenzene phase containing various concentrations of PBDO-700 (data are taken from Table 3.5).

% Extraction	D	Log[L*]	Log D
8.25	0.0899	-1.9477	-1.0462
16.28	0.1944	-1.6465	-0.7112
20.46	0.2572	-1.4704	-0.5897
20.68	0.2607	-1.2486	-0.5838
21.34	0.2713	-0.9477	-0.5666

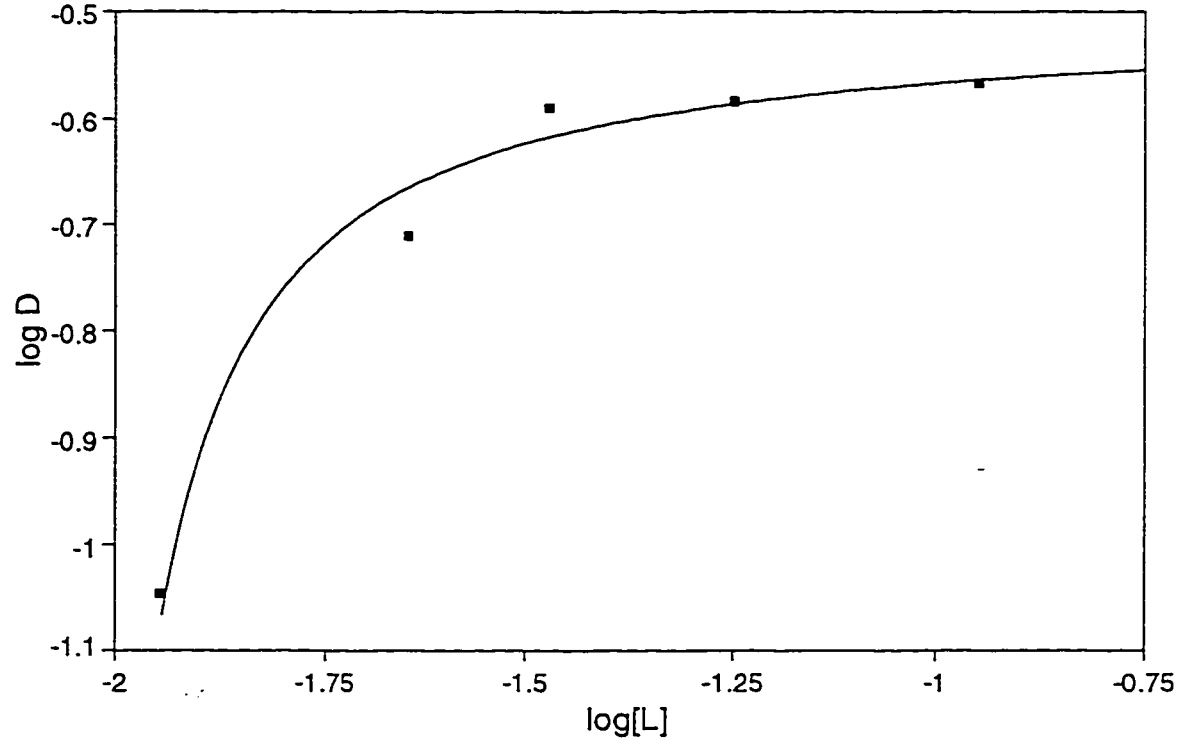


Fig 4.5 Log D versus log[L*] for Eu^{3+} extracted by PBDO-700 in nitrobenzene

Table 4.6 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations of PPG-1025 (data are taken from Table 3.6)

% Extraction	D	Log[L*]	Log D
0.60	0.0060	-2.0757	-2.2218
4.84	0.0509	-1.5591	-1.2933
10.34	0.1153	-1.3316	-0.9382
27.58	0.3808	-0.9880	-0.4193
58.92	1.4343	-0.5207	0.1566

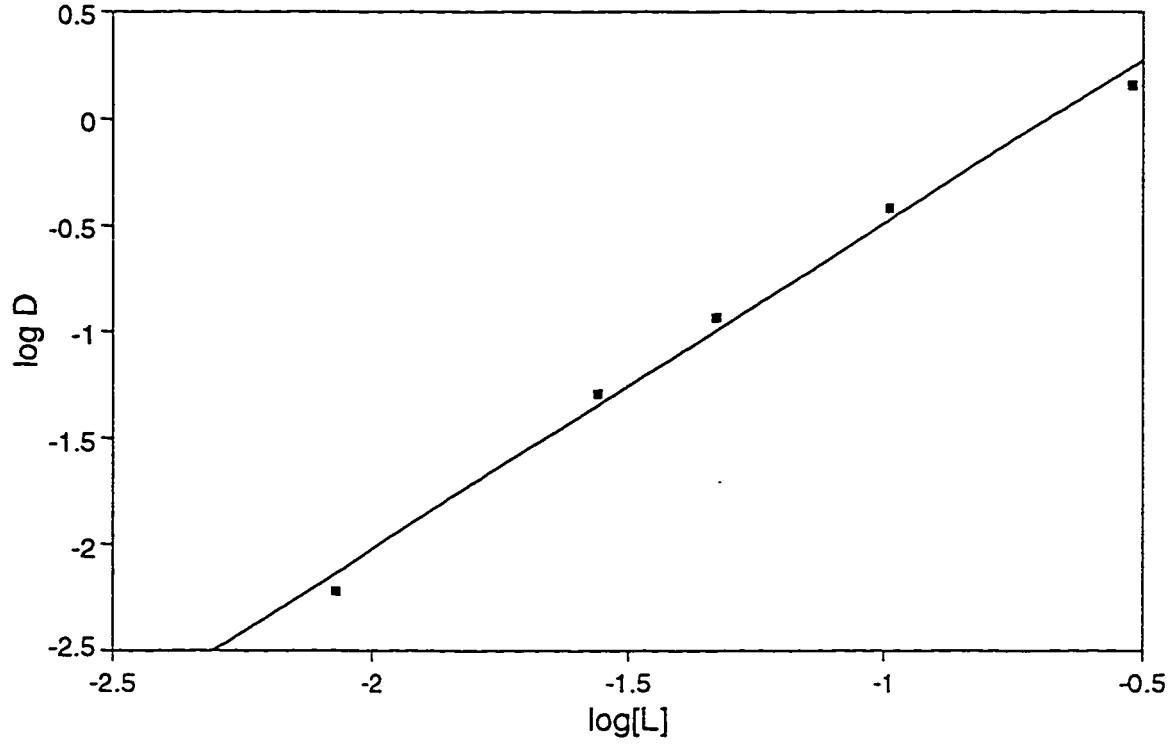


Fig 4.6 Log D versus log[L*] for Eu^{3+} extracted by PPG-1025 in 1,2-dichloroethane

Table 4.7 Extraction of Pr^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations of PPG-1025 (data are taken from Table 3.7)

% Extraction	D	Log[L*]	Log D
14.89	0.1750	-1.6946	-0.7570
22.12	0.2840	-1.3915	-0.5467
40.01	0.6669	-1.0016	-0.1759
58.89	1.4325	-0.6866	0.1561
67.11	2.0404	-0.5322	0.3097

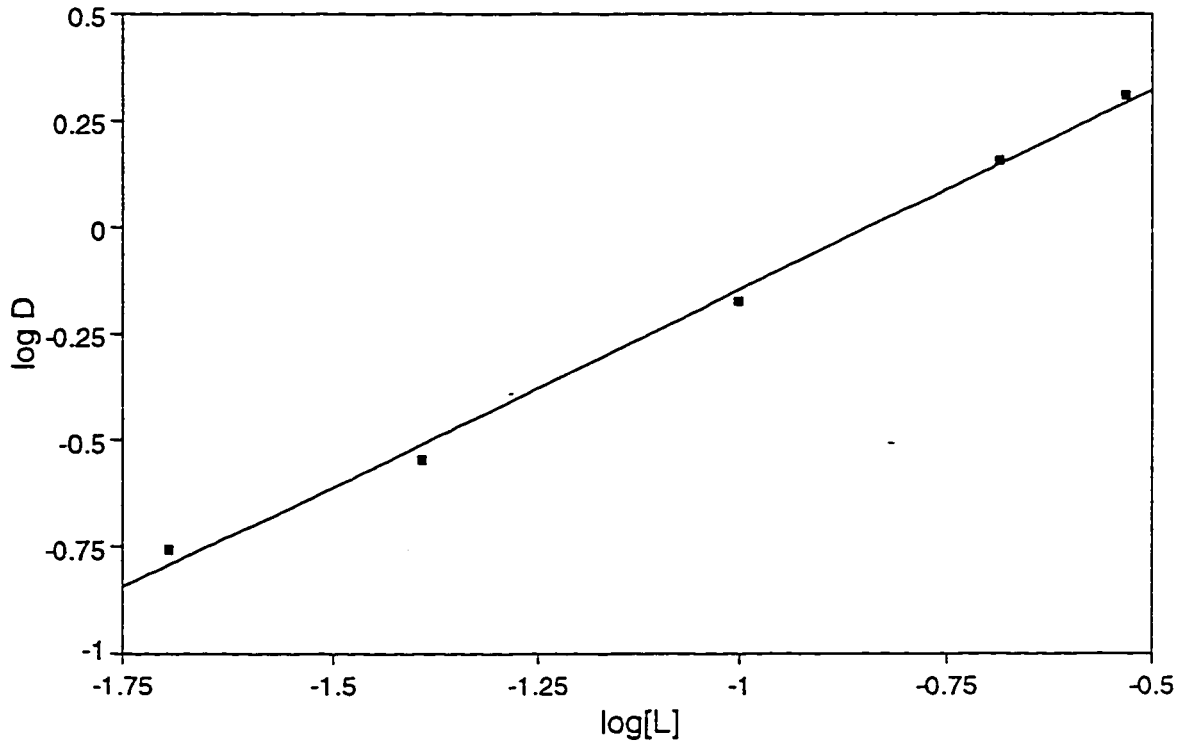


Fig 4.7 Log D versus log[L*] for Pr^{3+} extracted by PPG-1025 in 1,2-dichloroethane

Table 4.8 Extraction of Er^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations of PPG-1025 (data are taken from Table 3.8)

% Extraction	D	Log[L*]	Log D
2.03	0.0207	-2.0584	-1.6832
6.58	0.0704	-1.5144	-1.1524
10.09	0.1122	-1.3069	-0.9499
21.29	0.2704	-0.9154	-0.5679
39.54	0.6539	-0.5224	-0.1845

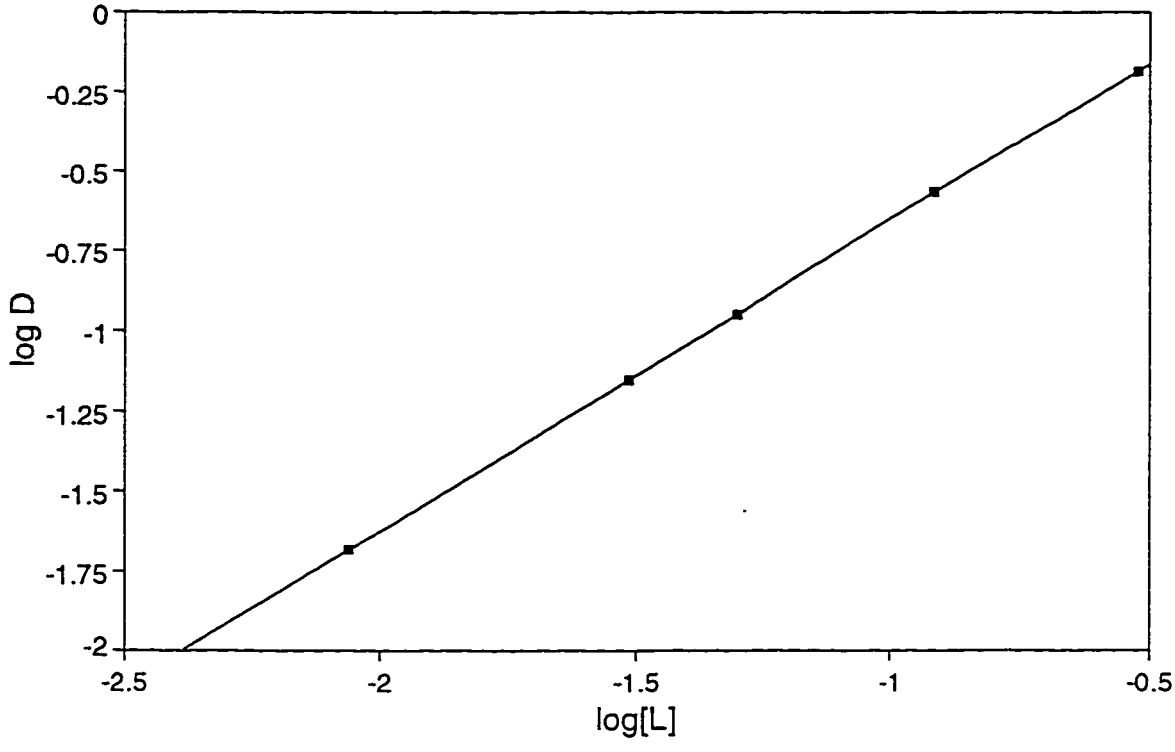


Fig 4.8 Log D versus log[L*] for Er^{3+} extracted by PPG-1025 in 1,2-dichloroethane

Table 4.9 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations of PEG-600 (data are taken from Table 3.9)

% Extraction	D	Log[L*]	Log D
2.00	0.0204	-1.6615	-1.6904
6.38	0.0681	-1.1838	-1.1668
9.46	0.1045	-0.9618	-0.9809
11.33	0.1278	-0.6608	-0.8935
14.00	0.1628	-0.5224	-0.7884

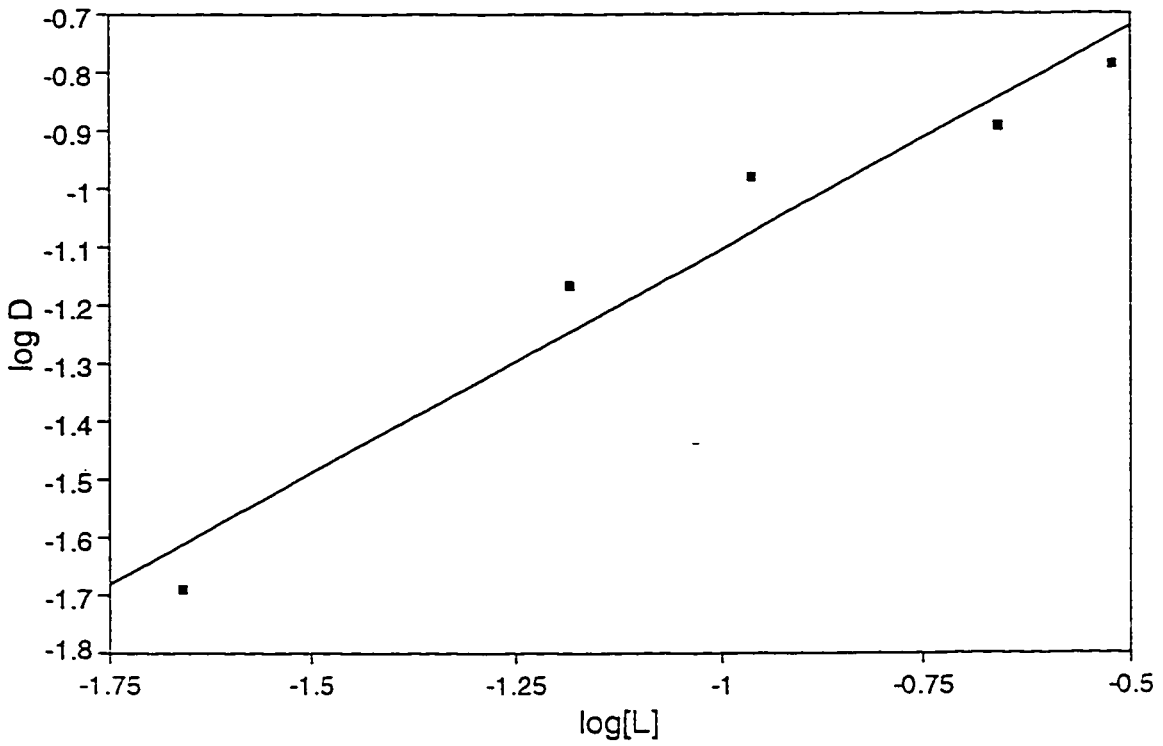


Fig 4.9 Log D versus log[L*] for Eu^{3+} extracted by PEG-600 in 1,2-dichloroethane

Table 4.10 Extraction of Eu^{3+} from aqueous medium containing 0.0555M picric acid into 1,2-dichloroethane phase containing various concentrations of PBDO-700 (data are taken from Table 3.10)

% Extraction	D	Log[L*]	Log D
3.85	0.0400	-1.9393	-1.3979
6.50	0.0698	-1.6383	-1.1561
6.14	0.0654	-1.4622	-1.1844
6.70	0.0718	-0.9393	-1.1439
6.80	0.0732	-0.5224	-1.1355

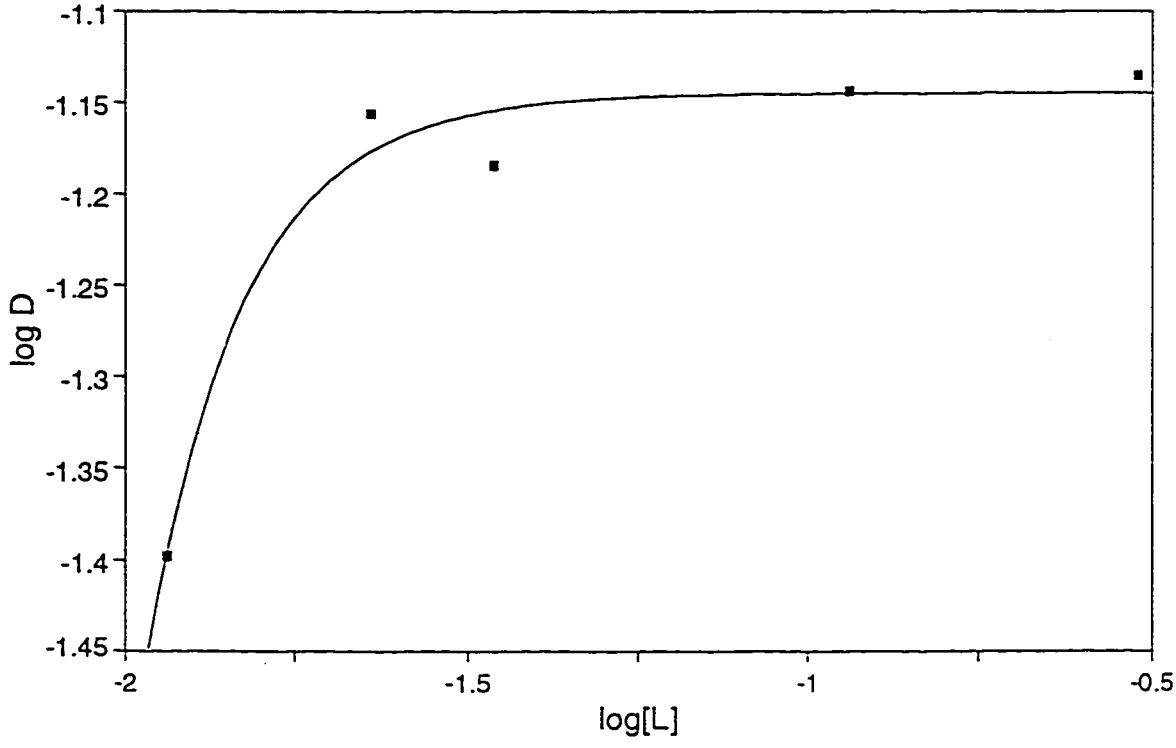


Fig 4.10 Log D versus log[L*]for Eu^{3+} extracted by PBDO-700 in 1,2-dichloroethane

Table 4.11 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentrations of PPG-1025 (data are taken from Table 3.33).

% Extraction	D	Log[L*]	Log D
37.38	0.5970	-1.6946	-0.2241
53.82	1.1654	-1.3915	0.0665
68.16	2.1407	-1.0061	0.3306
76.09	3.1824	-0.6866	0.5027
87.35	6.9051	-0.5322	0.8392

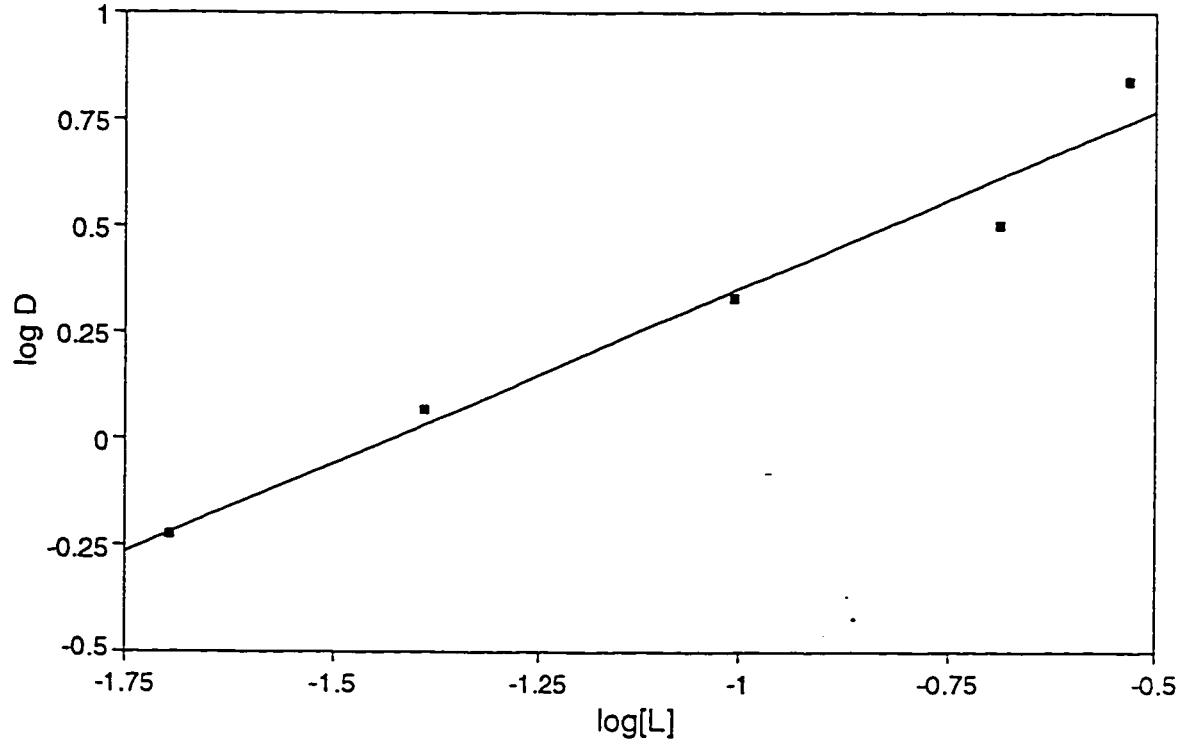


Fig 4.11 Log D versus log[L*] for Eu^{3+} extracted by PPG-1025 in 1,2-dichloroethane at pH 4.50

Table 4.12 Extraction of Pr^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentrations of PPG-1025 (data are taken from Table 3.35).

% Extraction	D	Log[L*]	Log D
42.66	0.7440	-2.0757	-0.1284
67.81	2.1066	-1.5591	0.3236
76.52	3.2589	-1.3316	0.5131
84.93	5.6357	-0.9880	0.7509
91.21	10.3766	-0.5207	1.0161

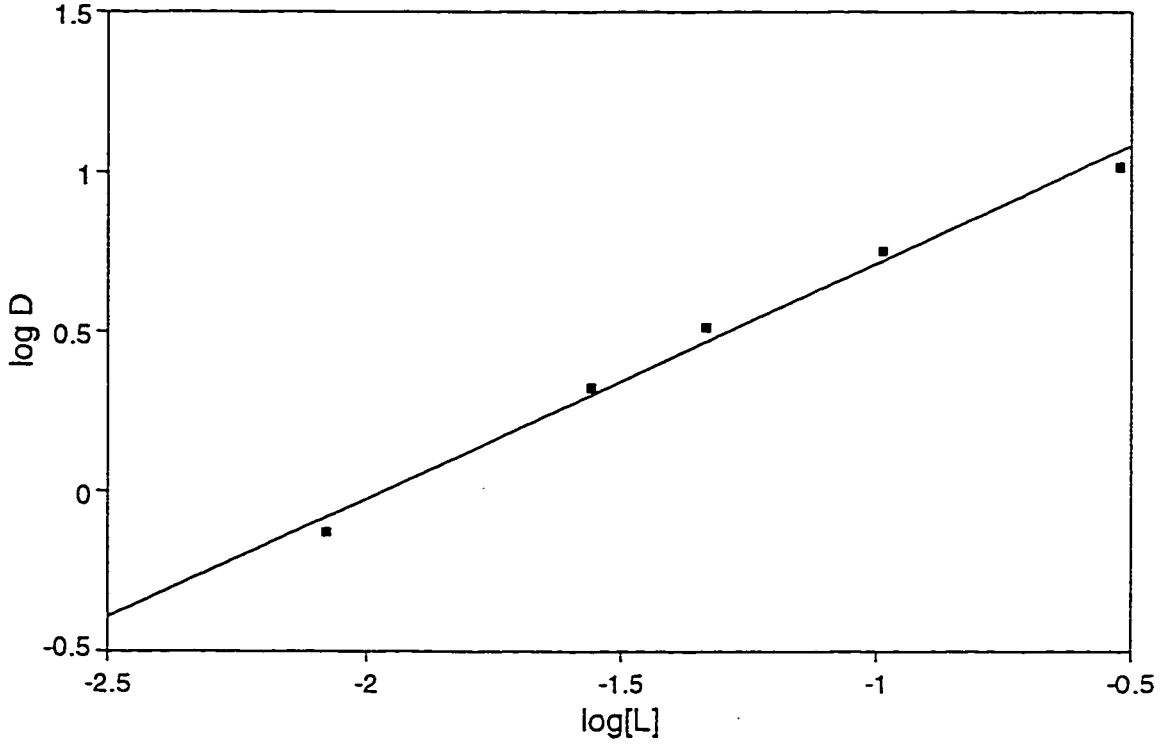


Fig 4.12 Log D versus log[L*] for Pr^{3+} extracted by PPG-1025 in 1,2-dichloroethane at pH 4.50

Table 4.13 Extraction of Er^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into nitrobenzene phase containing various concentrations of PPG-1025 (data are taken from Table 3.36).

% Extraction	D	Log[L*]	Log D
42.74	0.7466	-2.0605	-0.1269
68.72	2.1964	-1.5186	0.3417
72.38	2.6201	-1.3215	0.4183
75.01	3.0001	-0.9215	0.4772
80.34	4.0869	-0.5240	0.6114

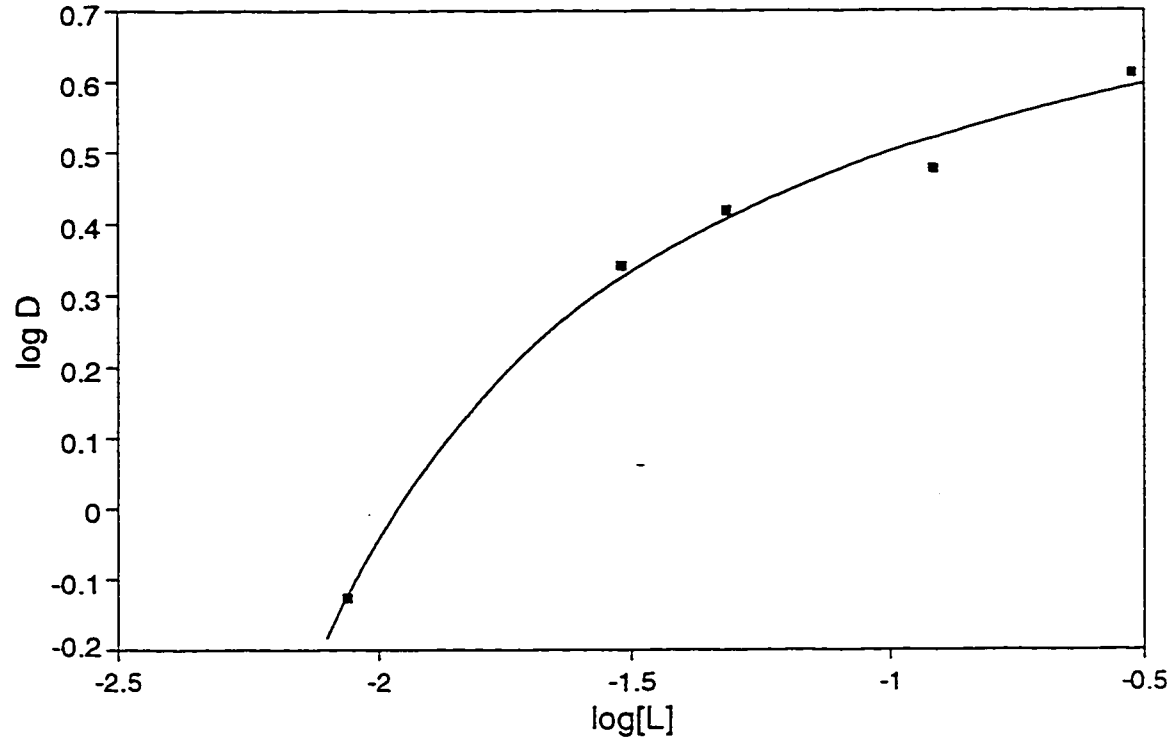


Fig 4.13 Log D versus log[L*] for Er^{3+} extracted by PPG-1025 in nitrobenzene at pH 4.50

Table 4.14 Extraction of Er^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentrations of PPG-1025 (data are taken from Table 3.37).

% Extraction	D	Log[L*]	Log D
8.18	0.0891	-2.0605	-1.0502
19.35	0.2399	-1.5258	-0.6199
24.88	0.3311	-1.3134	-0.4799
38.69	0.6310	-0.9154	-0.1999
61.43	1.2926	-0.5224	0.2021

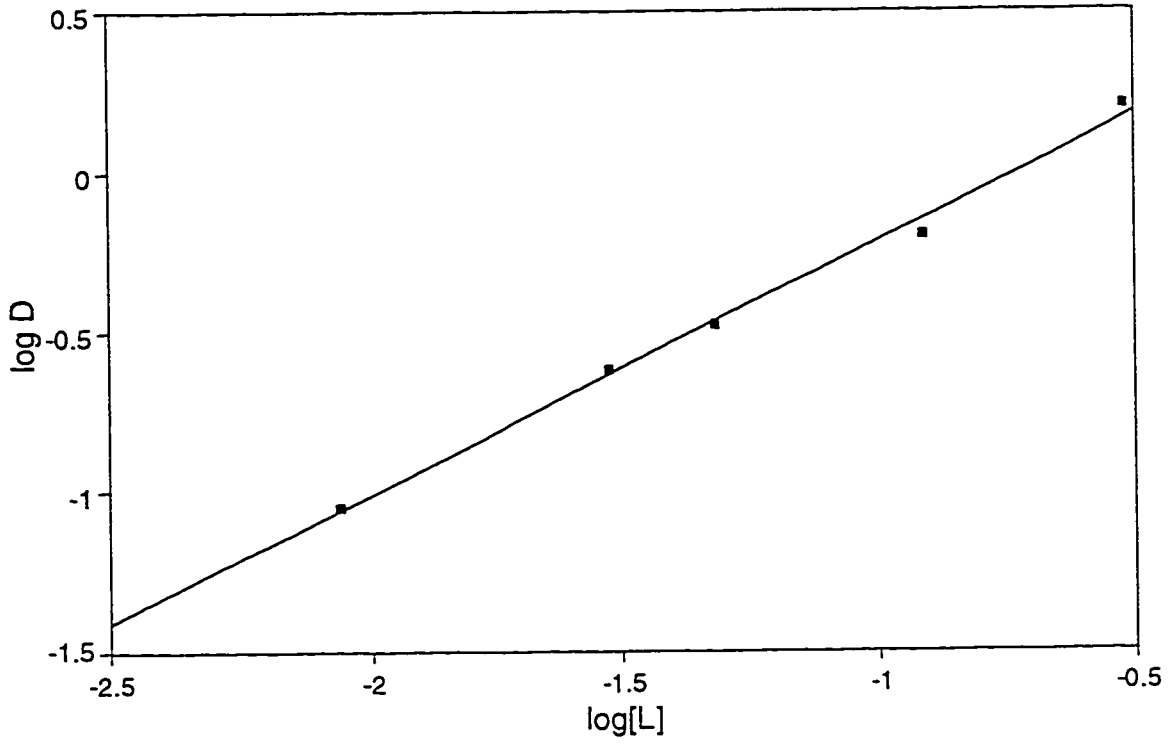


Fig 4.14 Log D versus log[L*] for Er^{3+} extracted by PPG-1025 in 1,2-dichloroethane at pH 4.50

Table 4.15 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentrations of PEG-600 (data are taken from Table 3.39).

% Extraction	D	Log[L*]	Log D
16.05	0.1912	-1.6615	-0.7185
33.22	0.4975	-1.1838	-0.3032
43.56	0.7718	-0.9618	-0.1125
53.56	1.1533	-0.6607	0.0619
60.00	1.5000	-0.5224	0.1761

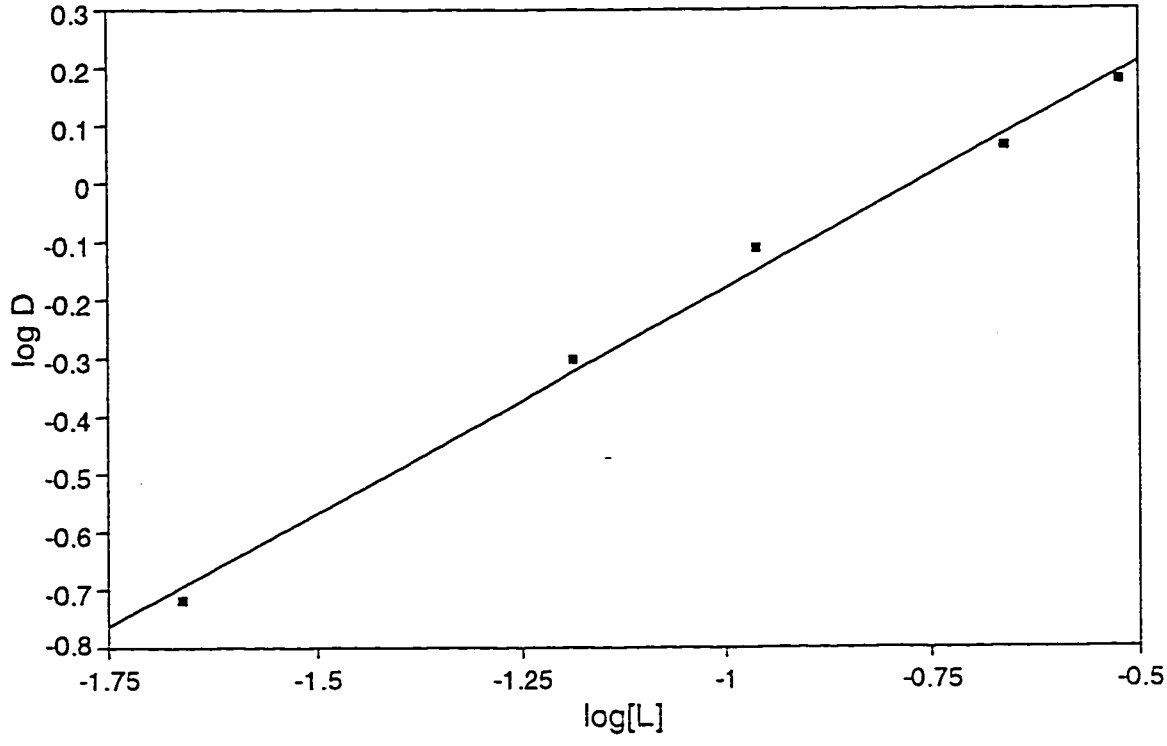


Fig 4.15 Log D versus log[L*] for Eu^{3+} extracted by PEG-600 in 1,2-dichloroethane at pH 4.50

Table 4.16 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into nitrobenzene phase containing various concentrations of PBDO-700 (data are taken from Table 3.40).

% Extraction	D	Log[L*]	Log D
32.98	0.4921	-1.9469	-0.3080
37.92	0.6108	-1.6459	-0.2141
47.80	0.9157	-1.4711	-0.0382
75.43	3.0700	-0.9477	0.4871
96.69	29.2115	-0.5345	1.4656

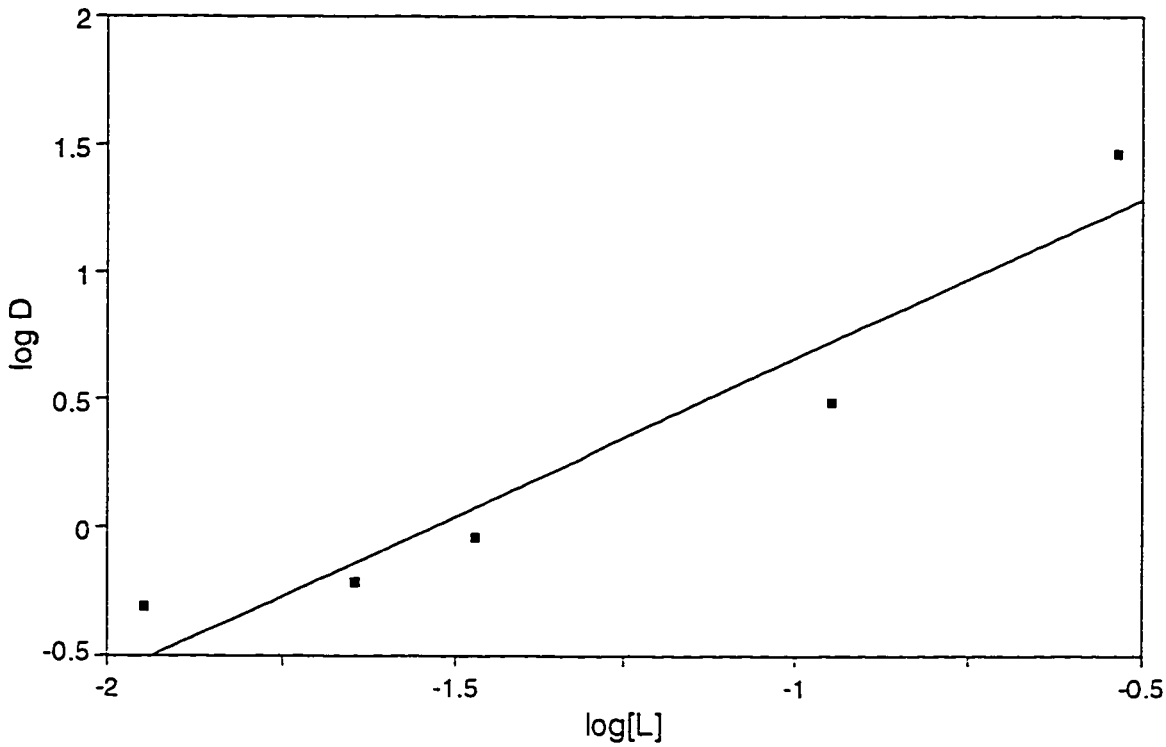


Fig 4.16 Log D versus log[L*] for Eu^{3+} extracted by PBDO-700 in nitrobenzene at pH 4.50

Table 4.17 Extraction of Eu^{3+} from aqueous medium containing 0.0546M picric acid at pH 4.50 into 1,2-dichloroethane phase containing various concentrations of PBDO-700 (data are taken from Table 3.41)

% Extraction	D	Log[L*]	Log D
4.00	0.0417	-1.9393	-1.3802
4.17	0.0435	-1.6383	-1.3614
6.64	0.0711	-1.4622	-1.1480
18.40	0.2255	-0.9393	-0.6469
61.06	1.5681	-0.5224	0.1954

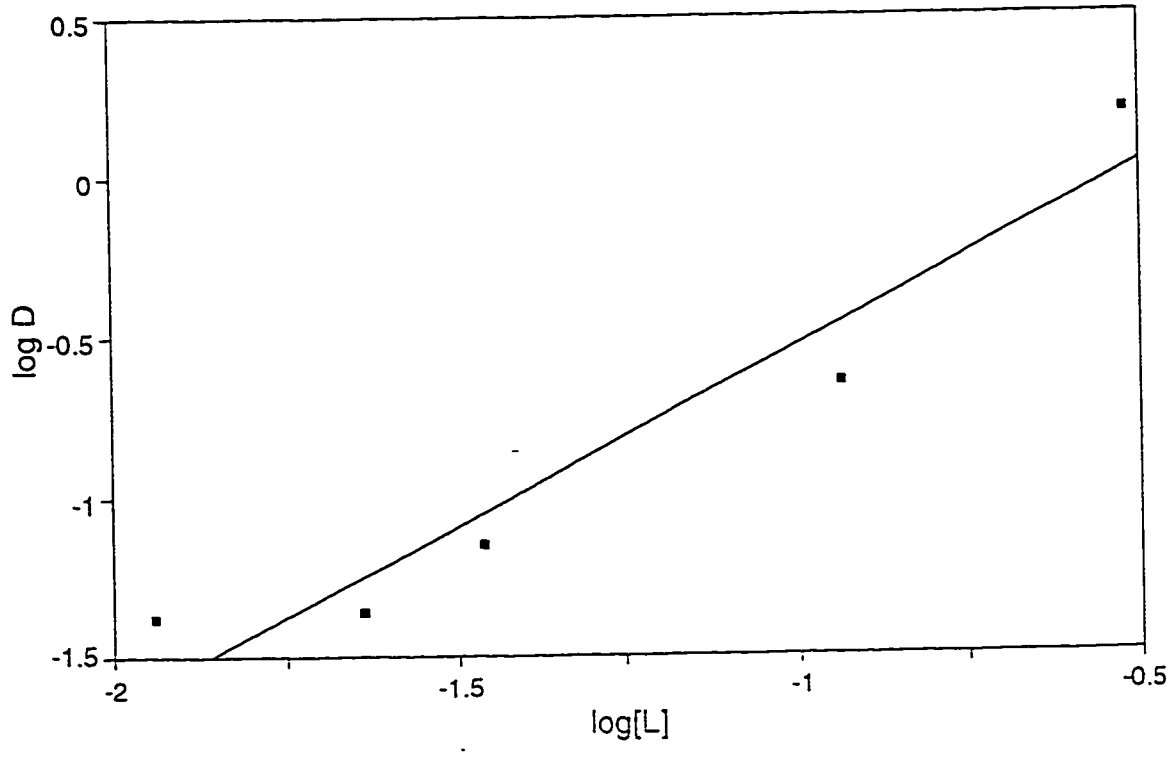


Fig 4.17 Log D versus log[L*] for Eu^{3+} extracted by PBDO-700 in 1,2-dichloroethane at pH 4.50

It is obvious from Table 4.18 that in the case of extractions involving PPG-1025 number of moles of propyleneoxide units associated with one mole of metals ion was between 13 to 14 units in spite of the very few cases (extraction of Eu^{3+}, Pr^{3+},and Er^{3+} from aqueous phases of pH<2 into 1,2-dichloroethane phase) in which odd results were obtained (Table 4.18). This stoichiometry was valid for all metal ions irrespective of the organic phase diluent.

Table 4.18 Number of moles of alkyleneoxide units binding with one mole of metal ion.

Polyoxyalkylene	Solvent	pH	Ion	Data from Table No.	Correlation Coefficient of variation	Slope	b
PPG-1025	NB	<2	Eu^{3+}	4.1	0.9955	0.8667	15.1
PPG-1025	NB	<2	Pr^{3+}	4.2	0.9915	0.8095	14.19
PPG-1025	NB	<2	Er^{3+}	4.3	0.9989	0.7816	13.6
PPG-1025	DCE	<2	Pr^{3+}	4.7	0.9976	0.9334	16.2
PPG-1025	DCE	<2	Er^{3+}	4.8	0.9999	0.9752	17.0
PPG-1025	DCE	4.60	Eu^{3+}	4.11	0.9821	0.8270	14.4
PPG-1025	DCE	4.60	Pr^{3+}	4.12	0.9945	0.7373	12.8
PPG-1025	NB	4.60	Er^{3+}	4.13	0.9915	0.7648	13.3
PPG-1025	DCE	4.60	Er^{3+}	4.14	0.9974	0.7954	13.8
PEG-600	NB	<2	Eu^{3+}	4.4	0.9928	0.6623	8.7
PEG-600	DCE	4.60	Eu^{3+}	4.15	0.9969	0.7764	10.2
PBDO-700	NB	<2	Eu^{3+}	4.5	0.9938	0.9731	9.7
PBDO-700	NB	4.60	Eu^{3+}	4.16	0.9999	1.004	10
PBDO-700	DCE	4.60	Eu^{3+}	4.17	0.9987	1.007	10

*NB= Nitrobenzene.

**DCE= 1,2-dichloroethane.

However, the number of ethyleneoxide units, in the case of extractions involving PEG-600, was found to be from 7 to 10 for Eu^{3+} . In the case of extraction Eu^{3+} by PBDO-700 in either nitrobenzene or 1,2-dichloroethane phases, the number of butadieneoxide units was about 10 in most cases studied indicating that the stoichiometry is almost 1:1 metal ion : PBDO-700. The percent extraction was reached into its limited level at the highest PBDO-700 concentration , thus this point has been excluded from the curve used to asses the stoichiometry.

The stoichiometry for alkali and alkaline earth metal ions with polyethylene glycol of the molar masses more than 400 was reported to be more than seven moles of ethylene units per a mole of metal ion[48]. However the stoichiometry for the tetraphenylborate salts of alkali and alkaline earth metal ion adducts of nononylphenoxy poly(ethyleneoxy) ethanol, polyethylene glycols and polypropylene glycols of alkylene oxide units were ranging from 17-4 propylene oxide units for PPG-1025 to 40 for nonylphenol derivatives of polyethylene glycol[6]. The stoichiometry was about 8.5 moles of EOU per a mole of sodium in the case of polyethylene glycol and its derivatives and 12 moles of alkyleneoxide (EOU or POU'S) per a mole of alkaline earth metal ion irrespective of the size of the ion. Obviously, in this study, the number of alkyleneoxide units per a mole of metal ion ,M^{3+}, is about 14 which may be quite consistent with the pervious reports.

4.3 Stoichiometry of $ML_{b/n}X_z$ Ion-pair with Respect to the Picrate Anion

The stoichiometry of the extracted Eu^{3+} ,Pr^{3+} and Er^{3+} picrate ion pairs has been estimated by extracting 100ppm of each of the various metal ions from aqueous phases containing varied concentrations of picric acid (from about 0.01M to about 0.05M) into organic phases of either nitrobenzene or 1,2-dichloroethane containing fixed concentration of polyoxyalkylene which was kept constant at a level of about 0.1M. Log D values were calculated for all cases and plotted against logarithm of picric acid concentrations according to the equation 4.12. The results are shown in Tables 4.19 to 4.28 and Figures 4.19 to 4.28.

All curves plotted for logD against log[picric acid] for all metal ions studied with the various polyoxyalkylenes indicate a linear relationship with correlation coefficient better than 0.99. Thus, according to equation 4.12, z, the number of moles of picrate associated with one mole of metal ion was estimated, and the results are summarized in Table 4.29. The total mean value for z is 3 , a value consistent with what is expected for a trivalent metal ion with a univalent anion. This confirms the validity of the model assumed for extraction.

Table 4.19 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1025M of PPG-1025 (data are taken from Table 3.11).

% Extraction	D	Log [picric acid]	Log D
8.56	0.0936	-1.9718	-1.0287
19.04	0.2352	-1.6706	-0.6286
31.00	0.4493	-1.4946	-0.3475
43.98	0.7851	-1.3410	-0.1051
52.46	1.1035	-1.2826	0.0428

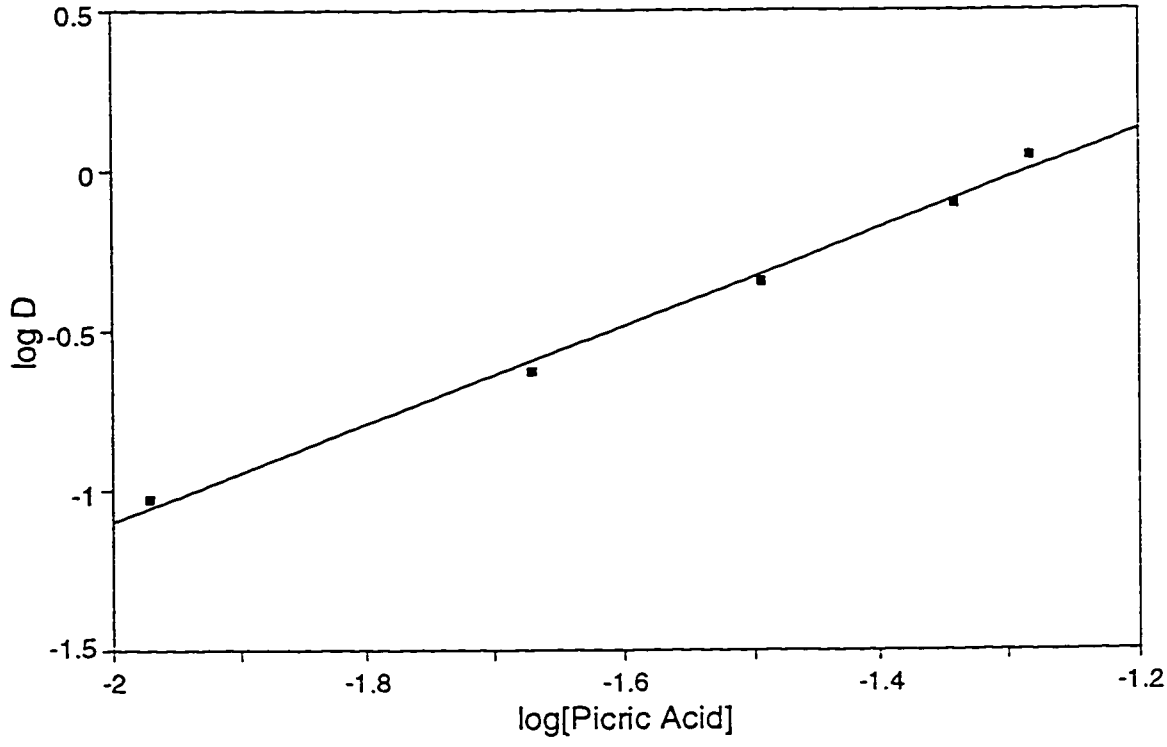


Fig 4.19 Log D versus log [picric acid] for Eu^{3+} extracted by PPG-1025 in nitrobenzene.

Table 4.20 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1025M of PPG-1025 (data are taken from Table 3.12).

% Extraction	D	Log [picric acid]	Log D
3.06	0.0316	-1.9718	-1.5008
9.05	0.0995	-1.6706	-1.0022
16.59	0.1989	-1.4946	-0.7014
23.18	0.3017	-1.3410	-0.5204
31.40	0.4577	-1.2826	-0.3394

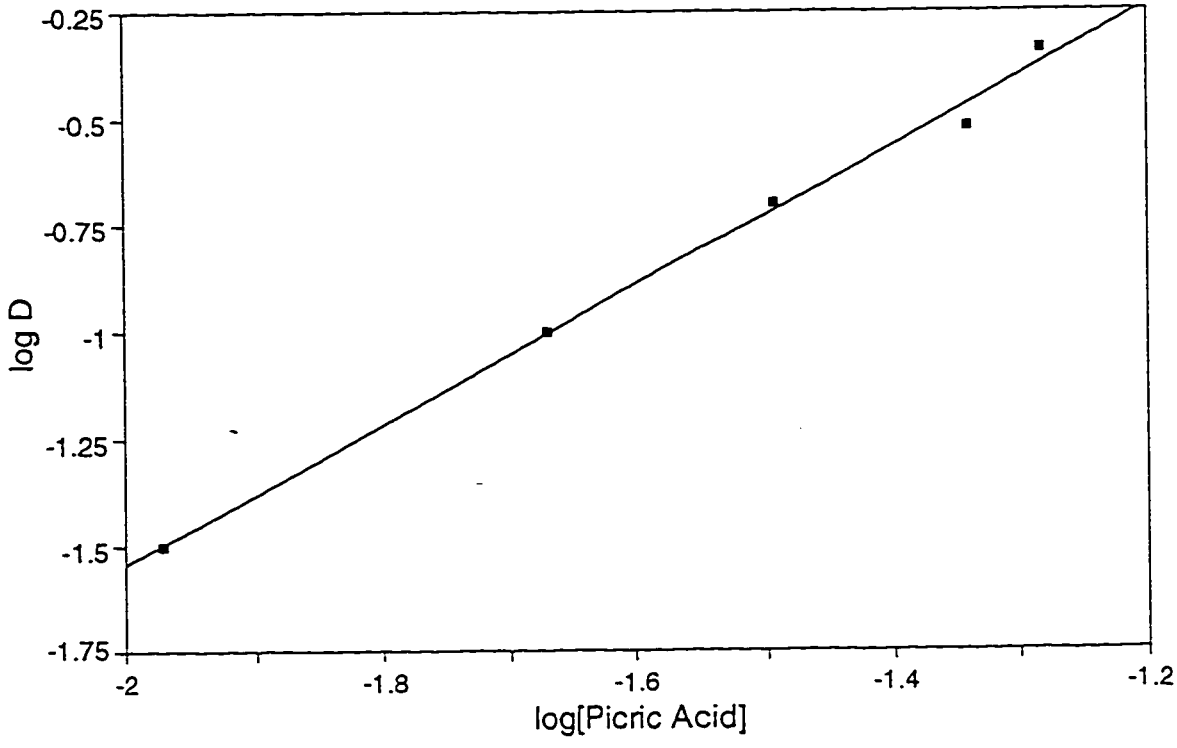


Fig 4.20 Log D versus log [picric acid] for Eu^{3+} extracted by PPG-1025 in 1,2-dichloroethan

Table 4.21 Extraction of Pr^{3+} from aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1030M of PPG-1025 (data are taken from Table 3.13).

% Extraction	D	Log [picric acid]	Log D
8.64	0.0948	-1.9439	-1.0242
20.54	0.2585	-1.6428	-0.5876
41.29	0.7033	-1.4667	-0.1529
51.84	1.0764	-1.3418	-0.0320
57.94	1.3776	-1.2811	0.1391

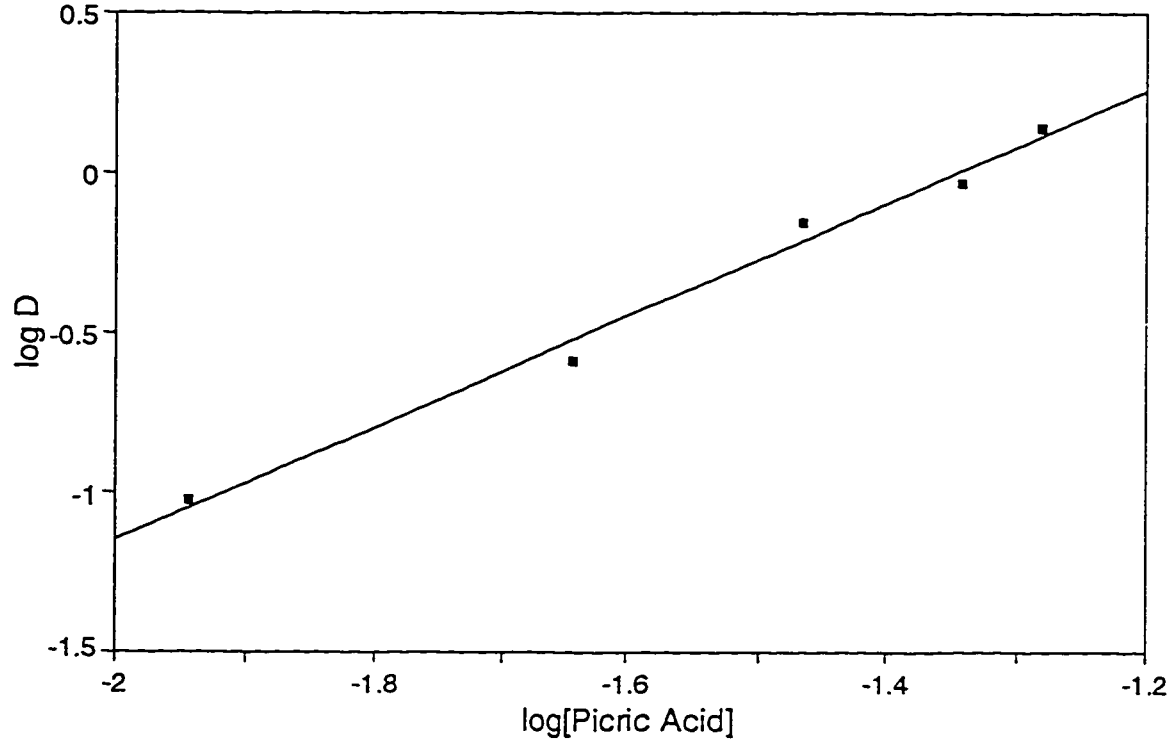


Fig 4.21 Log D versus log [picric acid] for Pr^{3+} extracted by PPG-1025 in nitrobenzene

Table 4.22 Extraction of Pr^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1028M of PPG-1025 (data are taken from Table 3.14).

% Extraction	D	Log [picric acid]	Log D
6.05	0.0644	-1.9439	-1.1911
14.39	0.1681	-1.6428	-0.7745
22.24	0.2860	-1.4667	-0.5436
30.14	0.4314	-1.3418	-0.3651
34.05	0.5163	-1.2811	-0.2871

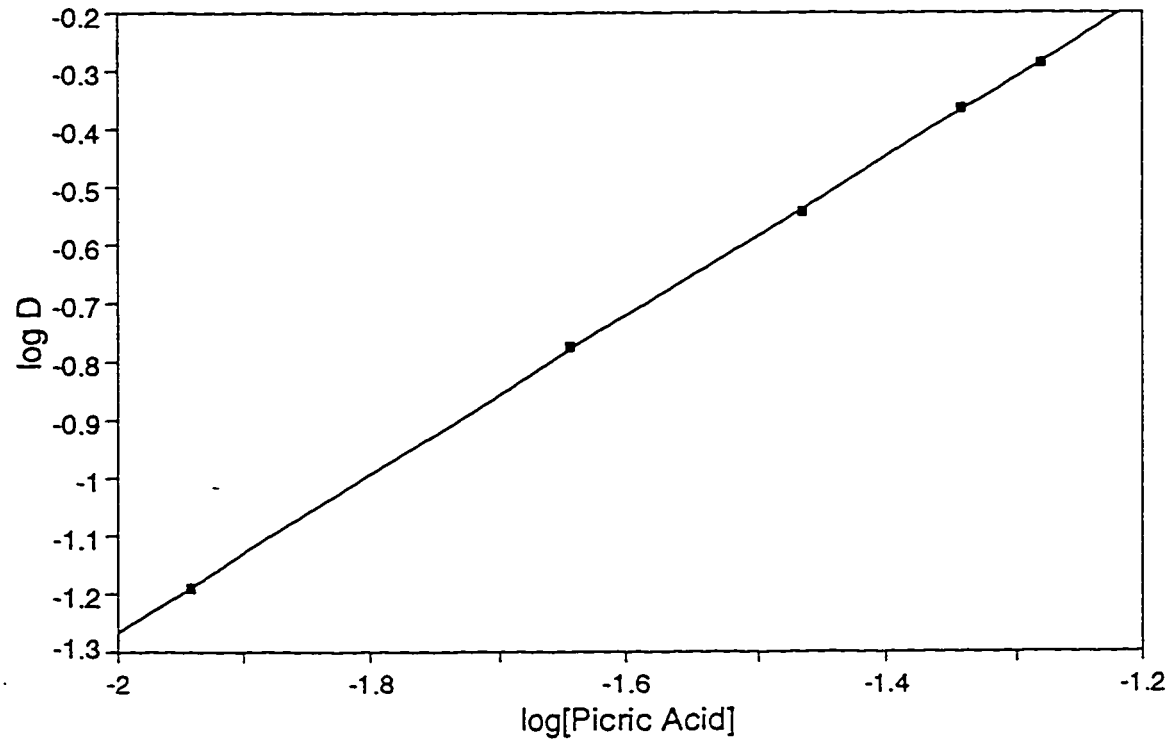


Fig 4.22 Log D versus log [picric acid] for Pr^{3+} extracted by PPG-1025 in 1,2-dichloroethane

Table 4.23 Extraction of Er^{3+} from aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1198M of PPG-1025 (data are taken from Table 3.15).

% Extraction	D	Log [picric acid]	Log D
9.09	0.1000	-1.9431	-1.0000
24.00	0.3158	-1.6421	-0.5006
37.20	0.5924	-1.4672	-0.2274
48.00	0.9231	-1.3418	-0.0348
55.00	1.2222	-1.2628	0.0872

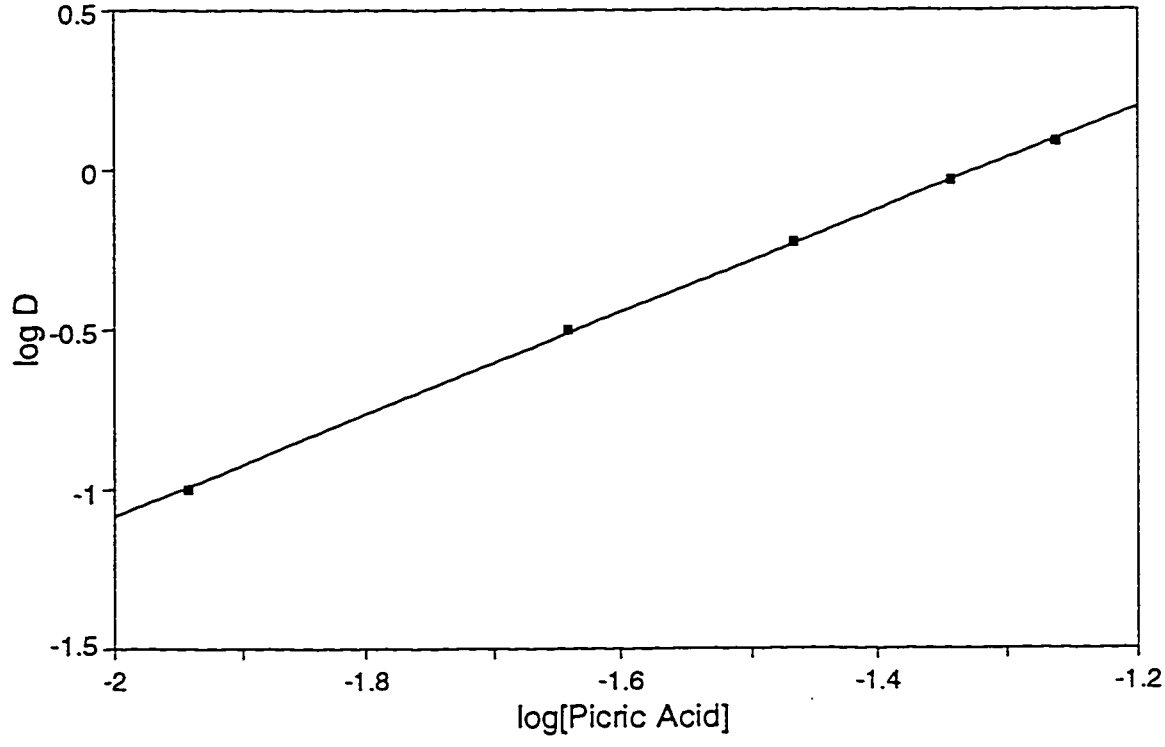


Fig 4.23 Log D versus log [picric acid] for Er^{3+} extracted by PPG-1025 in nitrobenzene

Table 4.24 Extraction of Er^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1215M of PPG-1025 (data are taken from Table 3.16).

% Extraction	D	Log [picric acid]	Log D
5.94	0.0632	-1.9431	-1.1996
15.20	0.1792	-1.6421	-0.7466
24.00	0.3158	-1.4672	-0.5006
32.90	0.4903	-1.3418	-0.3095
39.00	0.6393	-1.2628	-0.1943

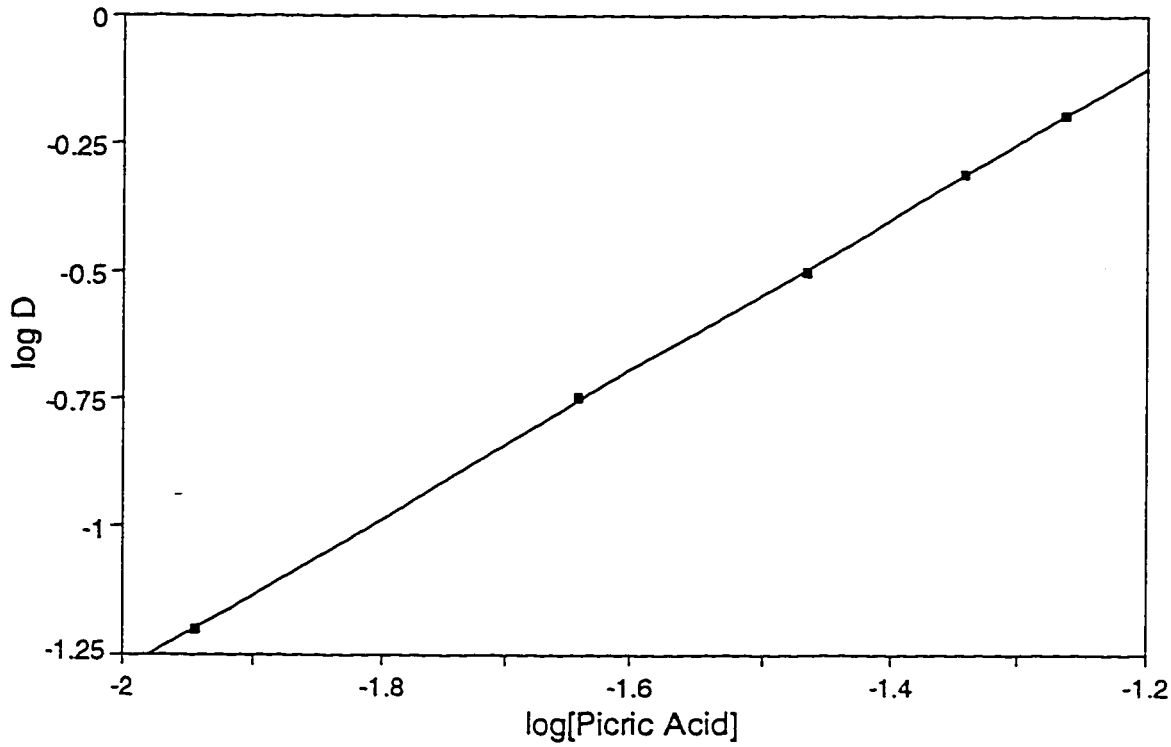


Fig 4.24 Log D versus log [picric acid] for Er^{3+} extracted by PPG-1025 in 1,2-dichloroethane

Table 4.25 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1125M of PEG-600 (data are taken from Table 3.17).

% Extraction	D	Log [picric acid]	Log D
6.47	0.0692	-1.9439	-1.1600
16.73	0.2009	-1.6428	-0.6970
28.47	0.3980	-1.4667	-0.4001
37.90	0.6103	-1.3418	-0.2145
44.84	0.8129	-1.2626	-0.0900

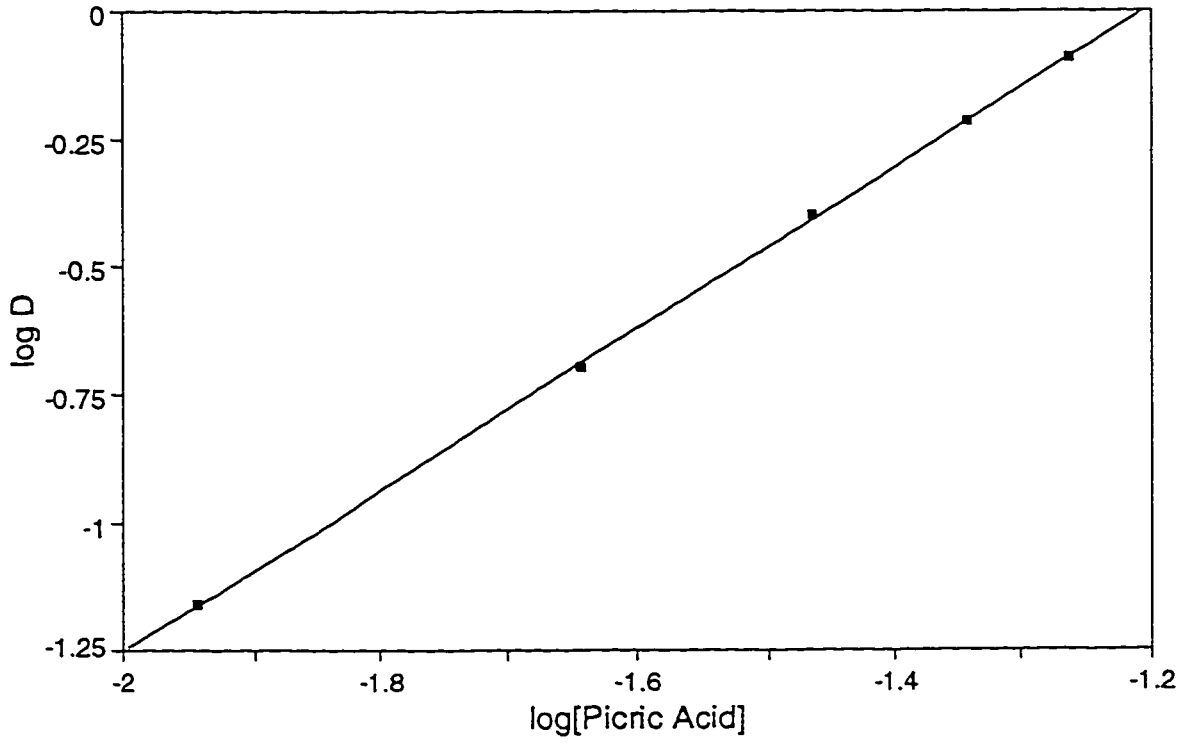


Fig 4.25 Log D versus log [picric acid] for Eu^{3+} extracted by PEG-600 in nitrobenzene

Table 4.26 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1035M of PEG-600 (data are taken from Table 3.18).

% Extraction	D	Log [picric acid]	Log D
7.36	0.0794	-1.9439	-1.0999
13.68	0.1585	-1.6428	-0.8000
25.31	0.3389	-1.4667	-0.4700
35.50	0.5504	-1.3418	-0.2593
38.21	0.6184	-1.2626	-0.2087

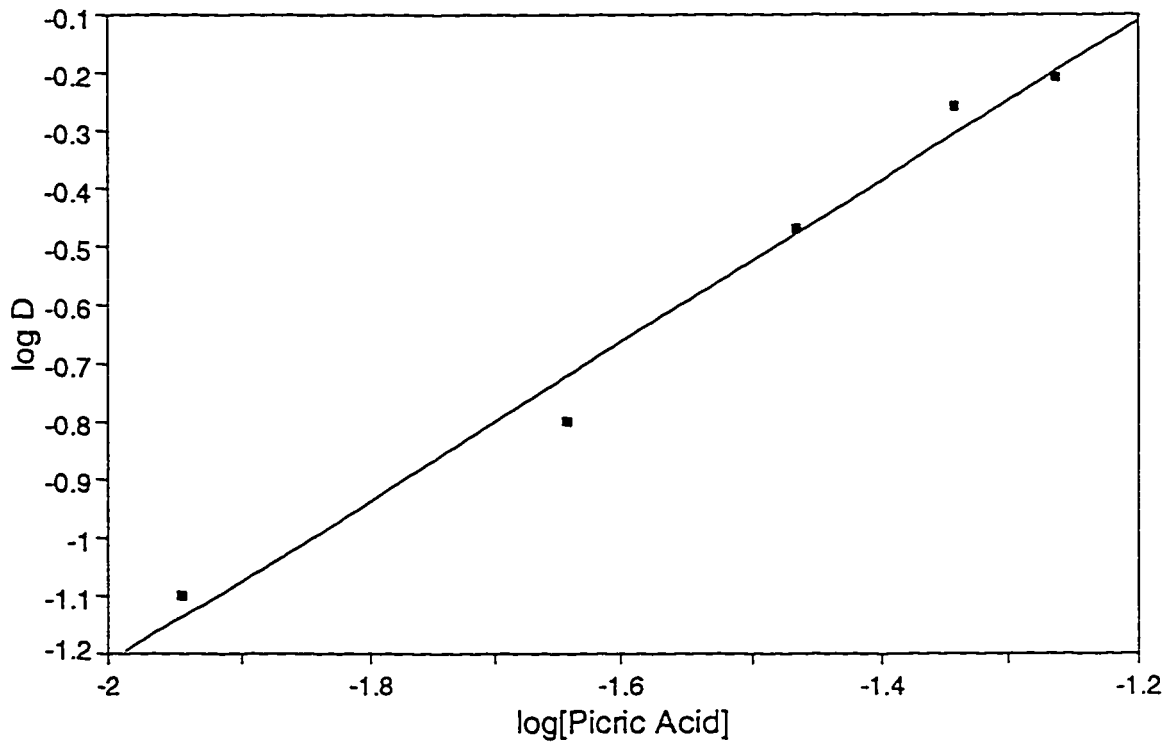


Fig 4.26 Log D versus log [picric acid] for Eu^{3+} extracted by PEG-600 in 1,2-dichloroethane

Table 4.27 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into nitrobenzene phase containing 0.1165M of PBDO-700 (data are taken from Table 3.19).

% Extraction	D	Log [picric acid]	Log D
2.06	0.0210	-1.9439	-1.6771
5.32	0.0562	-1.6428	-1.2503
9.09	0.1000	-1.4667	-1.0000
13.68	0.1585	-1.3418	-0.8000
20.08	0.2513	-1.2626	-0.5999

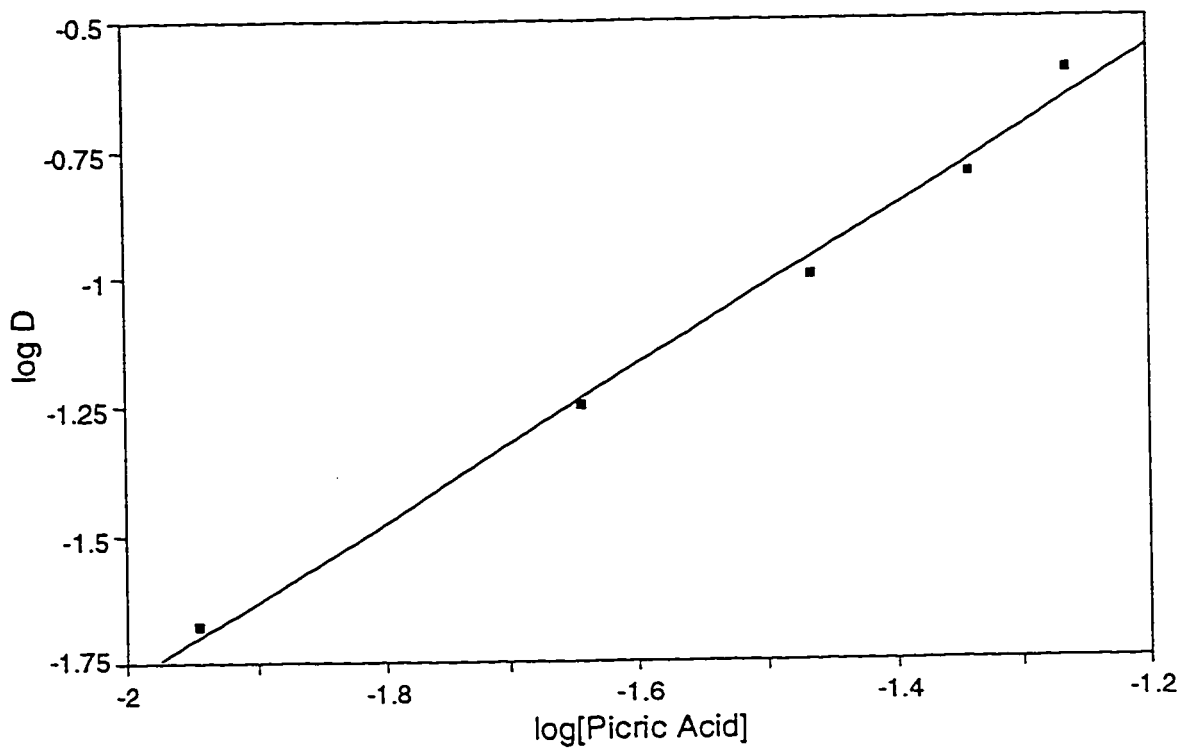


Fig 4.27 Log D versus log [picric acid] for Eu^{3+} extracted by PBDO-700 in nitrobenzene

Table 4.28 Extraction of Eu^{3+} from aqueous medium containing various concentrations of picric acid into 1,2-dichloroethane phase containing 0.1165M of PBDO-700 (data are taken from Table 3.20).

% Extraction	D	Log [picric acid]	Log D
0.65	0.0065	-1.9439	-2.1843
2.00	0.0204	-1.6428	-1.6902
3.20	0.0331	-1.4667	-1.4807
4.40	0.0460	-1.3418	-1.3370
5.45	0.0576	-1.2626	-1.2393

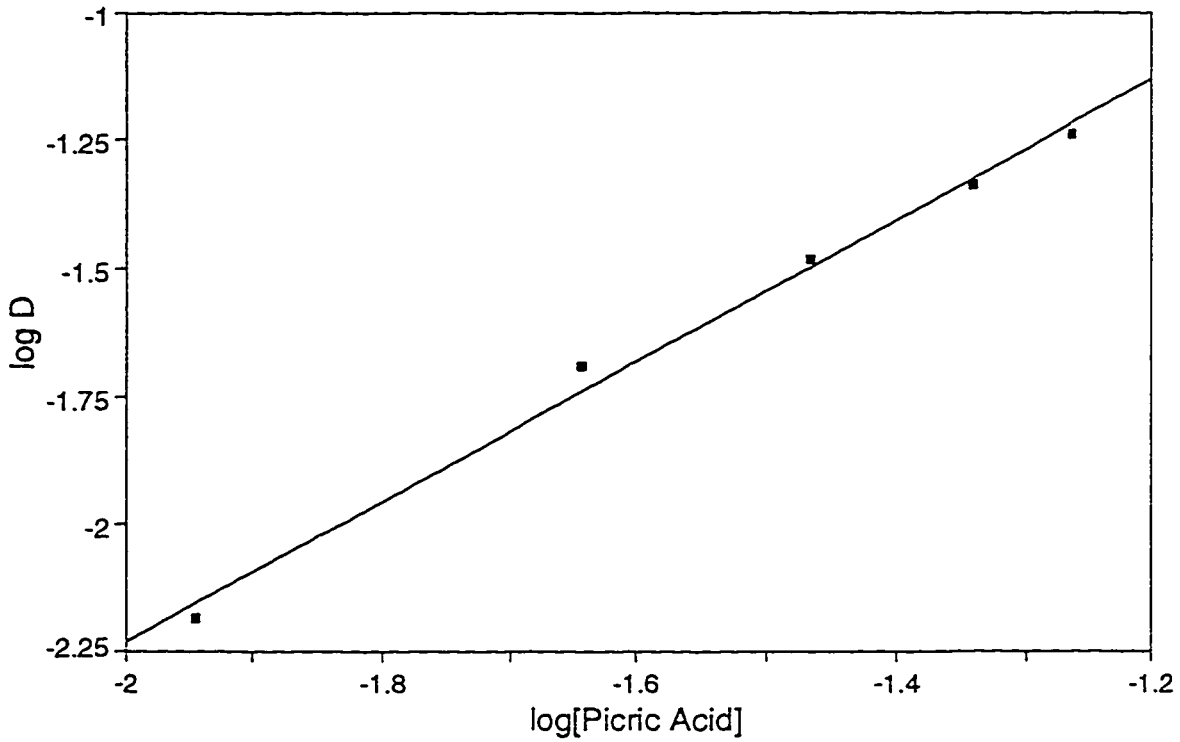


Fig 4.28 Log D versus log [picric acid] for Eu^{3+} extracted by PBDO-700 in 1,2-dichloroethane

Table 4.29 Number of moles of picrate anions (X^-) associated with one mole of metal in the ion-pair extracted by the various polyoxyalkylenes in either nitrobenzene or 1,2-dichloroethane.

Polyoxyal-kylene	Solvent	Metal	Figure	Correlation* Coefficient of variation	Slope	Z
PPG-1025	Nitrobenzene	Eu^{3+}	4.19	0.9969	1.53	3.06
PPG-1025	1,2-dichloroethane	Eu^{3+}	4.20	0.9975	1.63	3.26
PPG-1025	Nitrobenzene	Pr^{3+}	4.21	0.9939	1.75	3.50
PPG-1025	1,2-dichloroethane	Pr^{3+}	4.22	0.9994	1.36	2.72
PPG-1025	Nitrobenzene	Er^{3+}	4.23	0.9998	1.60	3.20
PPG-1025	1,2-dichloroethane	Er^{3+}	4.24	0.9999	1.47	2.94
PEG-600	Nitrobenzene	Eu^{3+}	4.25	0.9999	1.58	3.16
PEG-600	1,2-dichloroethane	Eu^{3+}	4.26	0.9913	1.38	2.76
PBDO-700	Nitrobenzene	Eu^{3+}	4.27	0.9962	1.53	3.06
PBDO-700	1,2-dichloroethane	Eu^{3+}	4.28	0.9962	1.38	2.76

Note:-

Both the correlation coefficients and slopes reported are taken from Figures 4.19 to 4.28.

4.4 Estimation of Log K_{ex} Values

Log K_{ex} values for the various metal ions with the polyoxyalkylenes studied have been estimated from equation 4.12 assuming that z=3 and K_a of picric acid = 0.513 and they are shown in Table 4.30 . It is obvious from Table 4.30 that log K_{ex} values estimated under same conditions of pH indicate same trend as mentioned previously for percent extractions. Log K_{ex} values for Pr^{3+}, Eu^{3+}, and Er^{3+} are 3.31, 3.20 and 2.77 respectively for the cases in which pH was not adjusted, nitrobenzene is the organic solvent; mean while the values increase when the pH is raised to 4.5 and they become 3.78, 3.51 and 2.91 respectively when 1,2-dichloroethane is the organic diluent . The separation factor (K^{I}_{ex} / K^{II}_{ex}) for Pr^{3+} / Eu^{3+}, Pr^{3+} / Er^{3+} and Eu^{3+} / Er^{3+} may be calculated as 1.29, 3.47 and 2.69 for unadjusted pH cases and nitrobenzene solvent and 1.90, 7.41 and 3.89 respectively for pH 4.50 and 1,2-dichloroethane organic solvent. Table 4.30 also indicates that log K_{ex} values for Eu^{3+} at pH without adjustment are 3.20, 2.52 and 3.18 for PPG-1025, PEG-600 and PBDO-700 respectively in nitrobenzene as the organic phase. This is consistent with the order of the percent extraction mentioned before. However, the percent extraction shows the superiority of PBDO-700 in nitrobenzene as the best extractant at the optimum range. Unfortunately, it was not possible to determine log K_{ex} values under these conditions since the percent extraction reached its maximum at the lowest polyoxyalkylene concentration.

Table 4.30 Log K_{ex} values for Eu^{3+}, Pr^{3+} and Er^{3+} extracted with various polyoxyalkylene concentration under different conditions.

Polyalkoxylate	Solvent	M^{3+}	pH	Log K_{ex}
PPG-1025	Nitrobenzene	Eu^{3+}	Not adjusted	3.20
PPG-1025	Nitrobenzene	Pr^{3+}	Not adjusted	3.31
PPG-1025	Nitrobenzene	Er^{3+}	Not adjusted	2.77
PPG-1025	1,2-dichloroethane	Eu^{3+}	4.50	3.50
PPG-1025	1,2-dichloroethane	Pr^{3+}	4.50	3.78
PPG-1025	1,2-dichloroethane	Er^{3+}	4.50	2.91
PEG-600	Nitrobenzene	Eu^{3+}	Not adjusted	2.52
PEG-600	1,2-dichloroethane	Eu^{3+}	4.50	2.94
PBDO-700	Nitrobenzene	Eu^{3+}	Not adjusted	3.18
PBDO-700	1,2-dichloroethane	Eu^{3+}	4.50	2.63

CONCLUSION

Three polyoxyalkylenes, namely polyethylene glycol-600, polypropylene glycol-1025 and polybutadiene oxide-700, have been tested as potent extractants for lanthanide metal ions represented by Pr^{3+} , Eu^{3+} and Er^{3+} from their aqueous solutions into organic phases containing the polyoxyalkylene ligands. The picrate concentration, pH of the aqueous phase and the organic solvent are the major parameters that affect the extraction of the various metal ions. The optimum picrate concentration should be as high as possible (~ 0.05M; the highest possible concentration) and the pH range was found to be from 3 - 5. Within these conditions the metals are extracted near quantitative into nitrobenzene organic phase which is more suitable foe extraction compared to organic phases of low dielectric constant such as 1,2-dichloroethane.

The polybutadiene oxide has achieved almost complete extraction for Pr^{3+} and Eu^{3+} in nitrobenzene. The tendency for extraction was found to be in the order of $Pr^{3+} > Eu^{3+} > Er^{3+} >$. Further more, the stoichiometry of the complexes extracted to the organic phases was estimated on the assumption that the picric acid concentration is much bigger than the concentration of metal ion, M^{3+} , in the aqueous phase and the polyoxyalkylene concentration in the organic phase is also much bigger than the metal ion concentration. The number of moles alkyleneoxide units associated with

each mole of metal ion was found to be about 14 units and each mole of metal ion in the ion-pair is associated with three moles of picrate anions.

This study can be extended for future investigations:

1. Polyoxyalkylenes of higher molar masses may used as extractants; these may achieve 100 percent extraction and improve the selectivity of extraction of the lanthanides or other metal ions.

2. Other lipophilic anions may be tested including thiocynate, perchlorate and dipicrylaminate.

3. Extractions of the lanthanide metal ions may also be tested in the presence of the other transition metal ions to determine the extraction selectivity of the polyoxyalkylenes towards the lanthanide metal ions.

4 Extraction of actinides as another group of the rare earth metal ions may also be tested.

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